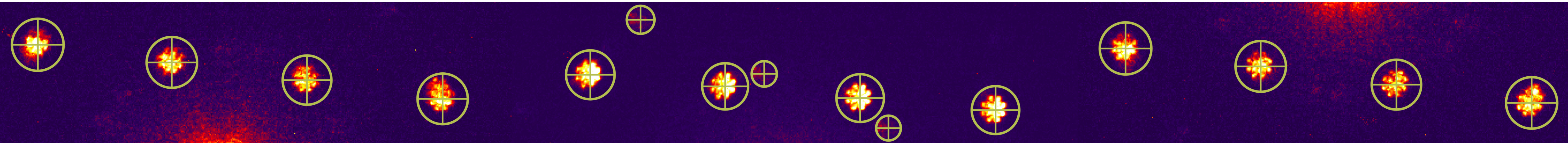
LA-UR-19-30501
Approved for public release; distribution is unlimited.

Title:	Strain and Isotopic Effects in Two-Dimensional WSe2
Author(s):	Pettes, Michael Thompson
Intended for:	Invited Seminar at North Carolina State University Mechanical Engineering Department, 2019-10-18 (Raleigh, North Carolina, United States)
Issued:	2020-07-02 (rev.1)

Strain and Isotopic Effects in Two-Dimensional WSe_2



Michael T. Pettes, Ph.D.

Scientist 3, MPA-CINT

October 18, 2019

Presentation to the Department of Mechanical and Aerospace Engineering

North Carolina State University

Raleigh, North Carolina 27695-7910

LA-UR-19-30501

CINT: A National User Facility for Nanoscience Research

CINT in Numbers

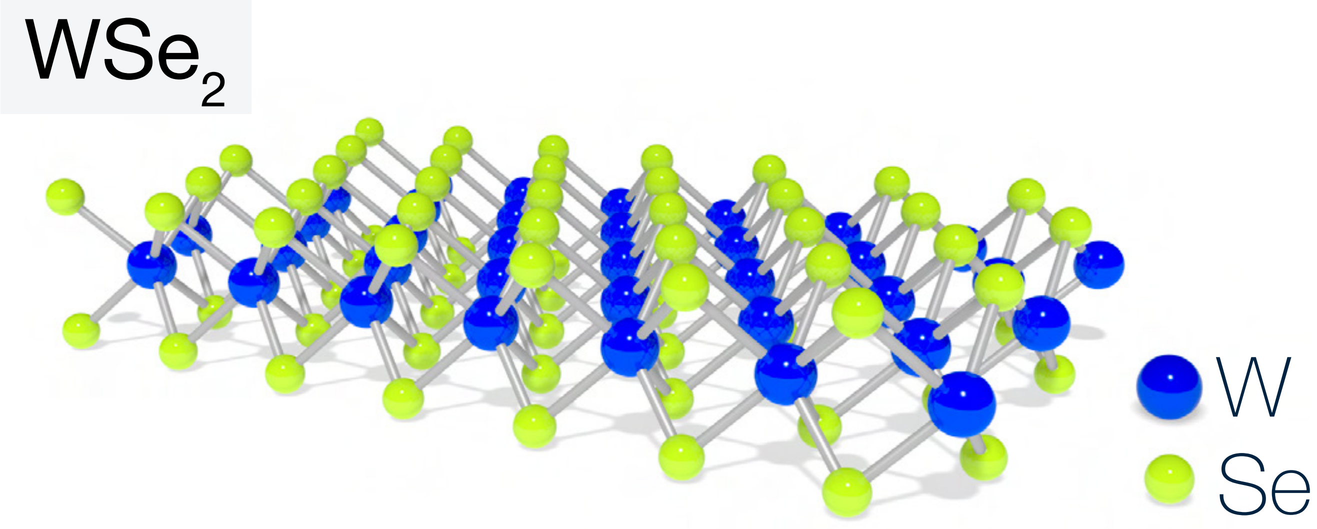
- 4 science thrusts
  - In Situ Characterization
  - Nano photonics
  - Quantum
  - Soft/Bio
- 2 facilities (LANL/SNL)
- 51 staff scientists
- 32+ postdocs and grad students
- 650+ users
- 200+ projects
- 300+ publications/year
- $0, no fee for pre-competitive research
- 100% full recovery cost for proprietary research
- **Questions:** hdbrown@sandia.gov

The 2019 fall call for user proposals is open March 1-31, 2020.

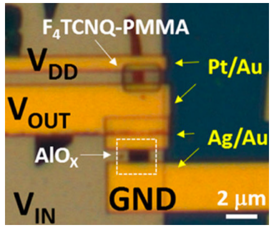
https://cint.lanl.gov/

Background: Lots of 2D materials, why WSe_2?

- *n*- and *p*-type doping
- $m_{electron} \sim m_{hole}$
- ~50-200 $cm^2V^{-1}s^{-1}$ mobility
- Band edges aligned with common metal work functions
- Useful in many important future application areas:

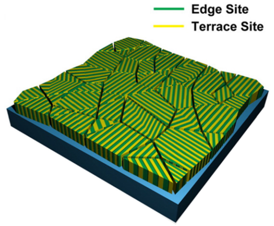


Electronics



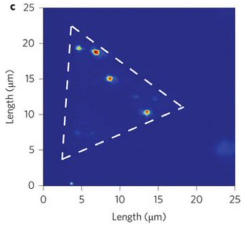
Yu & Palacios 2015
http://dx.doi.org/10.1021/acs.nanolett.5b00668

Electrocatalysis



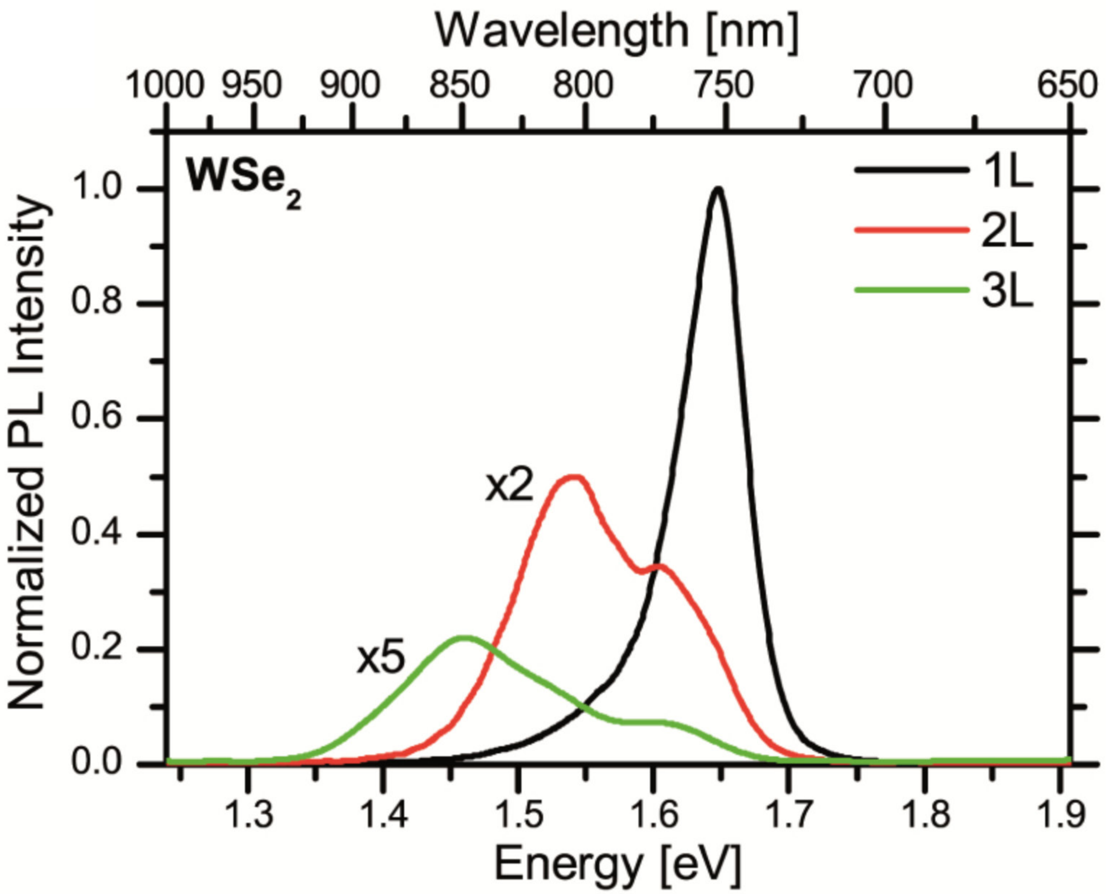
Wang & Cui 2013
http://dx.doi.org/10.1021/nl401944f

Quantum Optics



He 2015
https://doi.org/10.1038/nnano.2015.75

Background: Band structure evolution



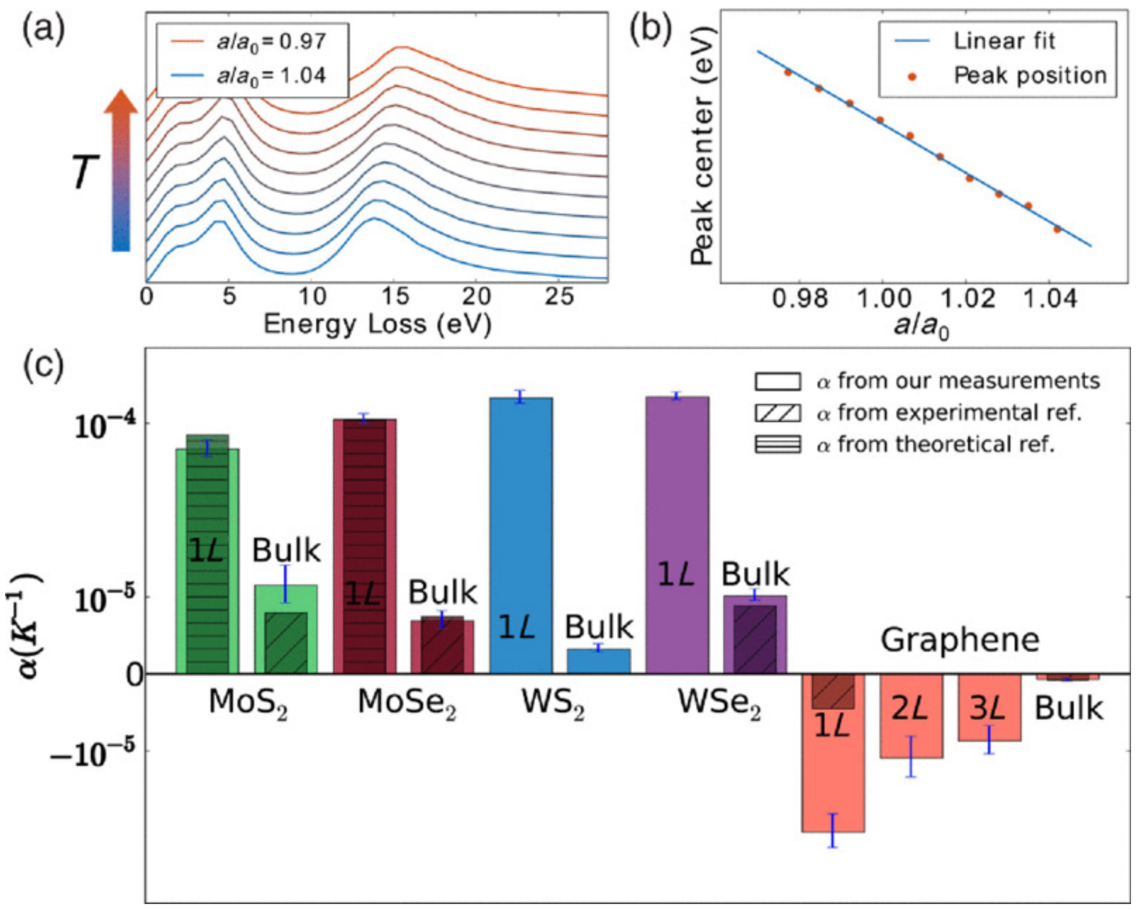
Tonndorf & Bratschitsch 2013, https://doi.org/10.1364/OE.21.004908

- Bulk WSe_2 is an indirect semiconductor
  - $E_{g,\mathrm{indirect}}$ = 1.2 eV (1.03 µm)
- Trilayer is indirect
  - $E_{g,\mathrm{indirect}}$ = 1.46 eV (849 nm)
  - $E_{g,\mathrm{A}}$ = ~1.60 eV (773 nm)
- Bilayer is indirect
  - $E_{g,\mathrm{indirect}}$ = 1.54 eV (806 nm)
  - $E_{g,\mathrm{A}}$ = 1.60 eV (773 nm)
- Monolayer is a direct semiconductor
  - $E_{g,\mathrm{A}}$ = 1.65 eV (752 nm)

Strain-coupled Transport in Bi-layer WSe_2

Motivation: 2D materials much more compliant than bulk

Thermal Expansion Coefficient, 2D >> bulk



Hu & Klie 2018, https://doi.org/10.1103/PhysRevLett.120.055902

relationship between thermal expansion coefficient, *α*, and elastic modulus, *E*:

$$\alpha \propto \gamma \rho c_v / E$$

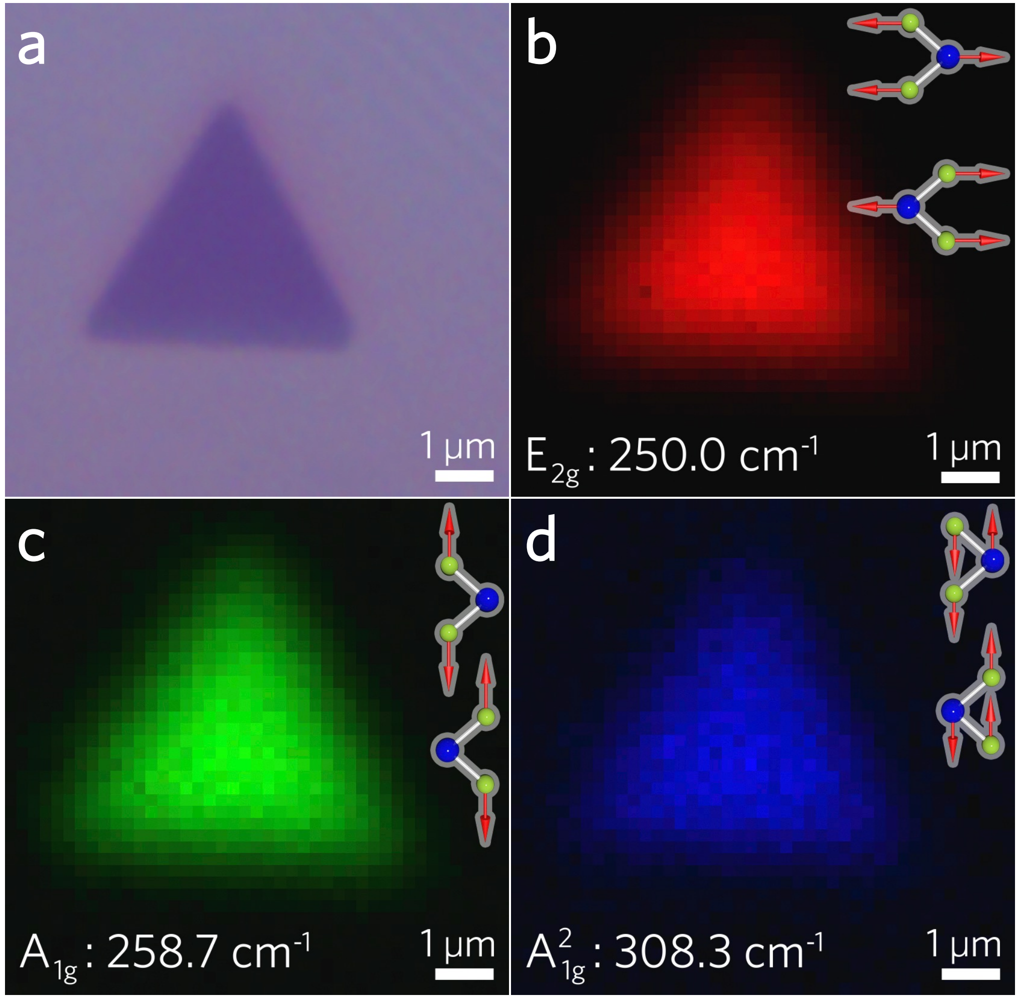
so with assumptions

$$E \propto \alpha^{-1}$$

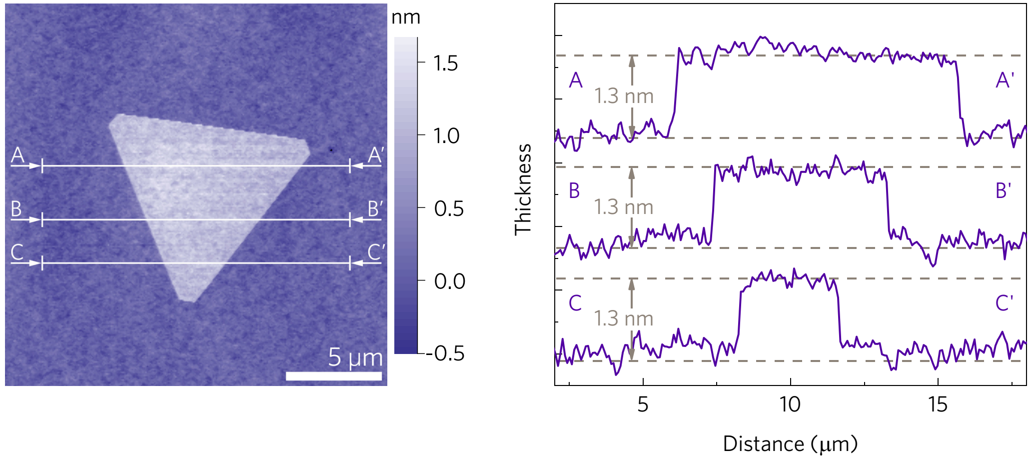
- (α , E) of PET substrate:
  - 20-80×10^{-6} K^{-1}, (2–4) GPa
- (α , E) of WSe_2
  - monolayer: 154×10^{-6} K^{-1}
  - bilayer: 42×10^{-6} K^{-1}
  - bulk: (7–14)×10^{-6} K^{-1}, ~170 GPa

Spatial uniformity of synthesized bilayer WSe_2

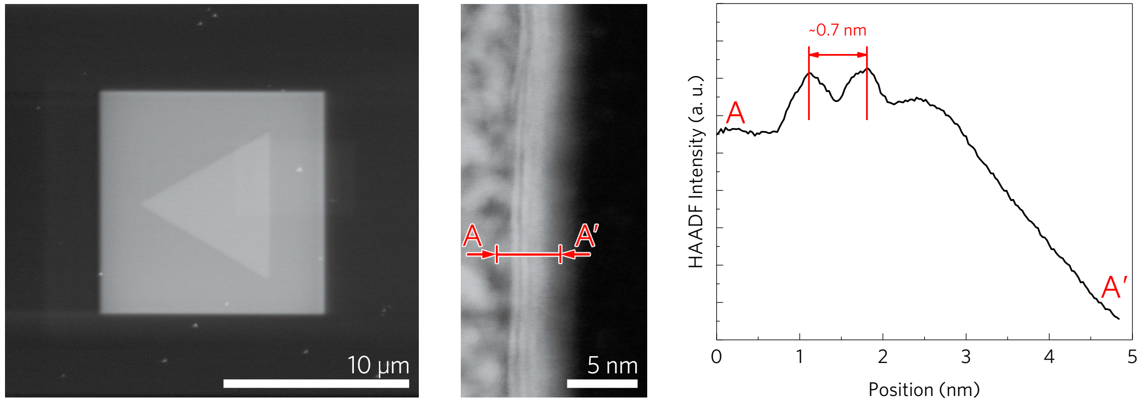
Raman – excitation @ 532 nm



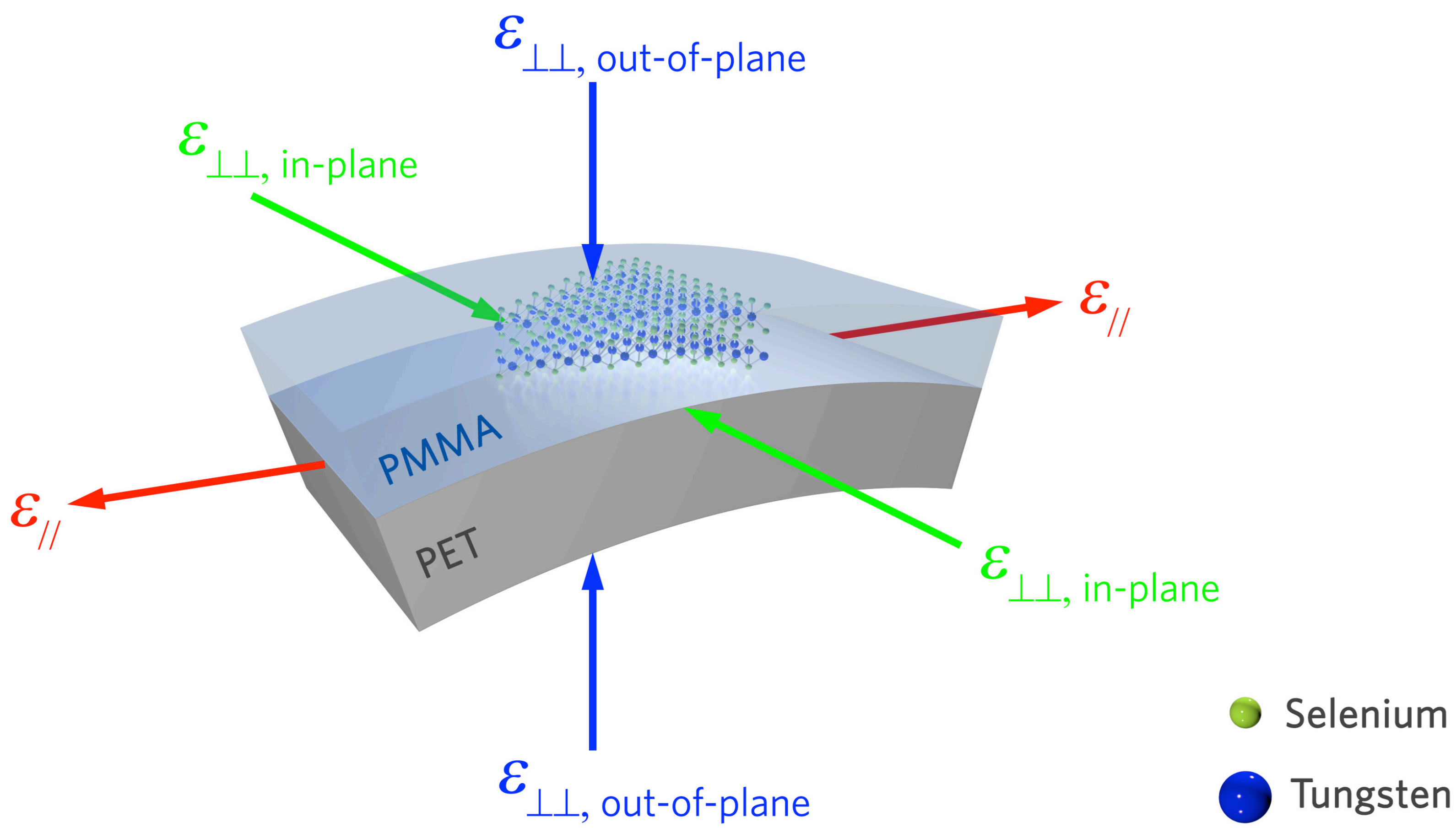
Atomic Force Microscopy

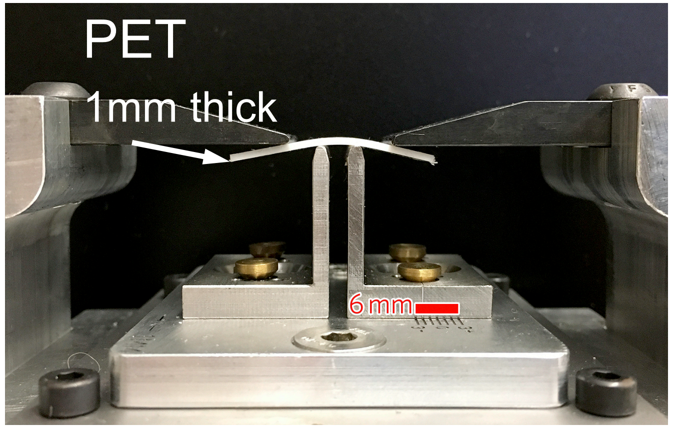


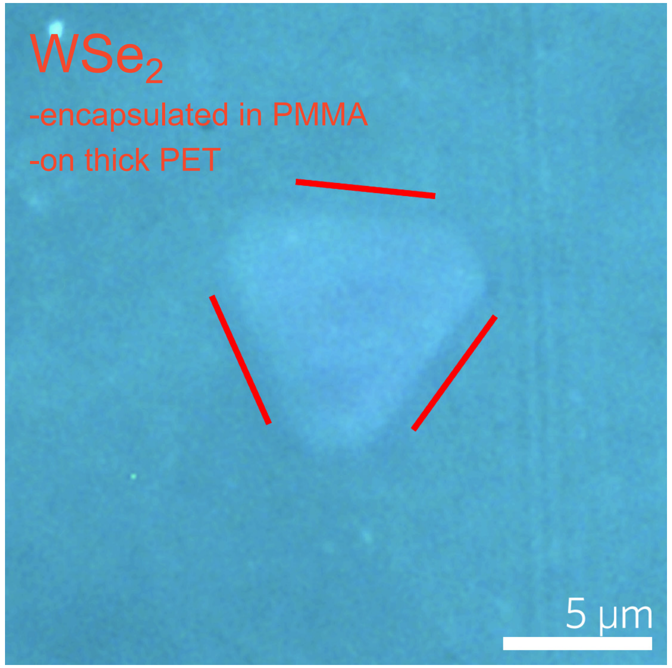
Corrected STEM using TEAM 0.5, 80 kV (w/Peter Ercius, NCEM)



A four point bending approach to impart strain





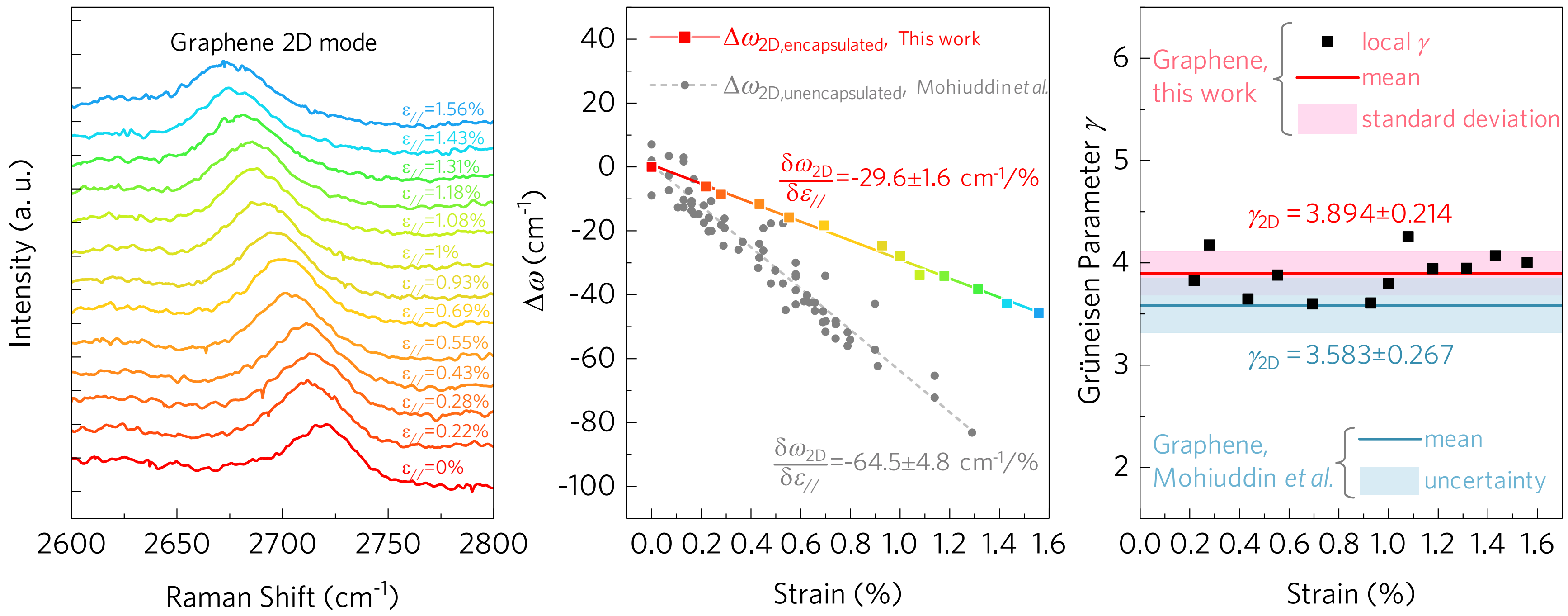


Validation of our strain values: Encapsulated monolayer graphene

Measured Grüneisen parameter of CVD graphene

$$\gamma = V\left(\frac{\partial P}{\partial E}\right)_V = \frac{V}{C_V}\left(\frac{\partial S}{\partial V}\right)_T$$

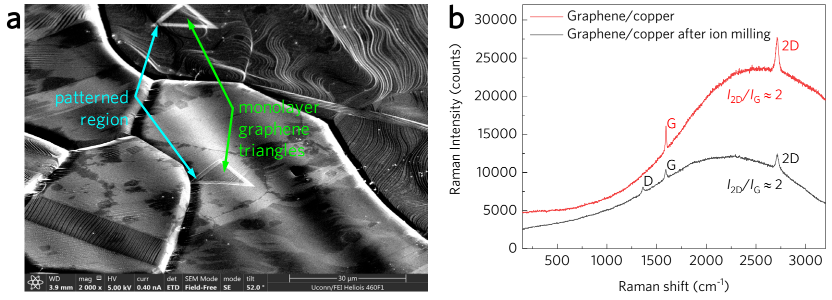
$$\gamma_i = \begin{cases} -\dfrac{\Delta\omega_{0,i}^{+} + \Delta\omega_{0,i}^{-}}{2\varepsilon_{//}(1-\nu_{\text{in-plane}}-\nu_{\text{out-of-plane}})\omega_{0,i}}, & i = E_{2g} \\ -\dfrac{\Delta\omega_{0,i}}{\varepsilon_{//}(1-\nu_{\text{in-plane}}-\nu_{\text{out-of-plane}})\omega_{0,i}}, & i = A_{1g}, A_{1g}^{2} \end{cases}$$

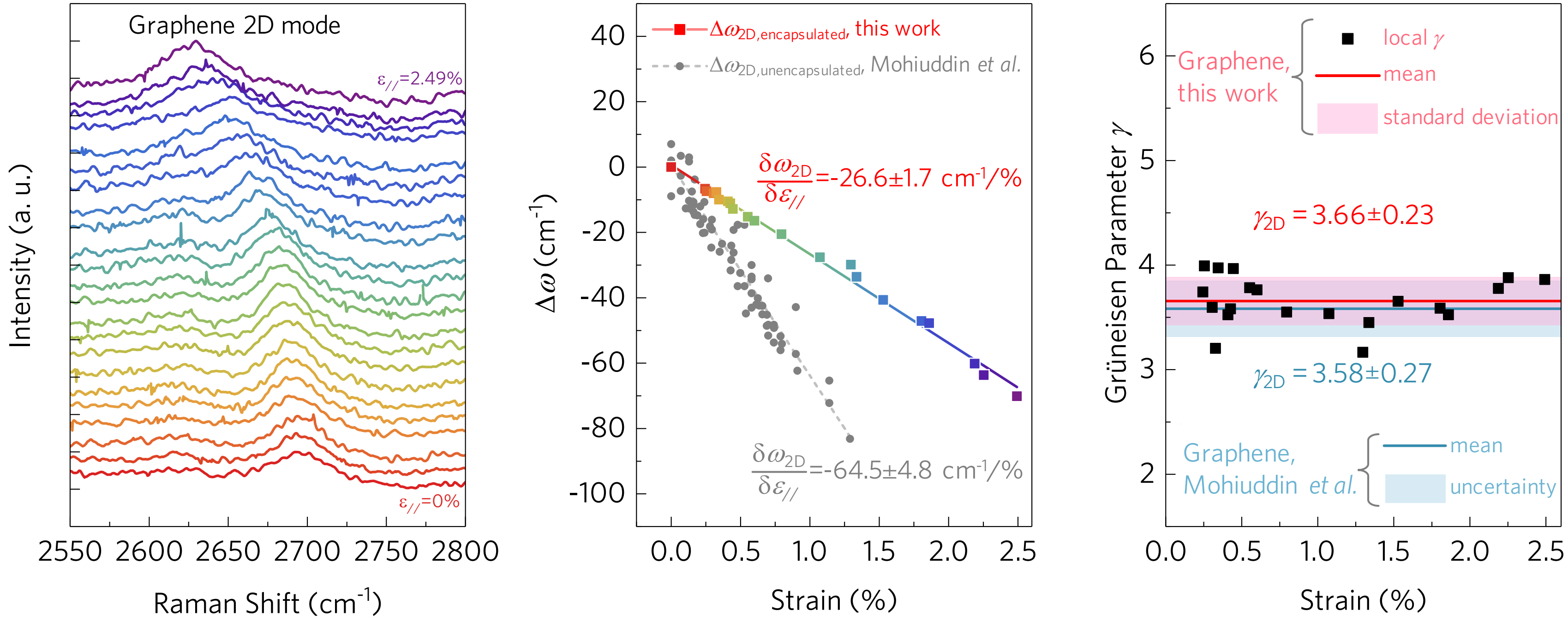


We compare our work with Mohiuddin & Ferrari et al., *Phys. Rev. B* 2009, *79*, 205433. https://doi.org/10.1103/PhysRevB.79.205433

Validation of our strain values: Patterned and encapsulated monolayer graphene

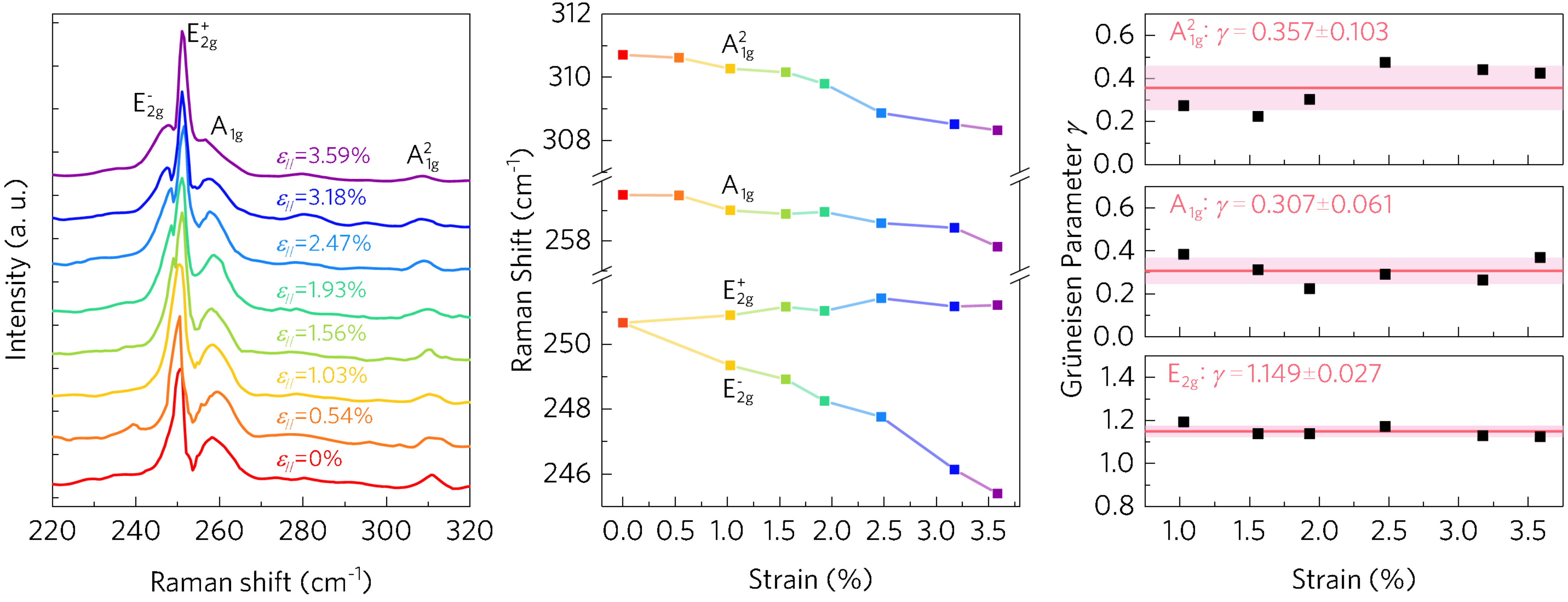
Measured Grüneisen parameter of patterned CVD graphene



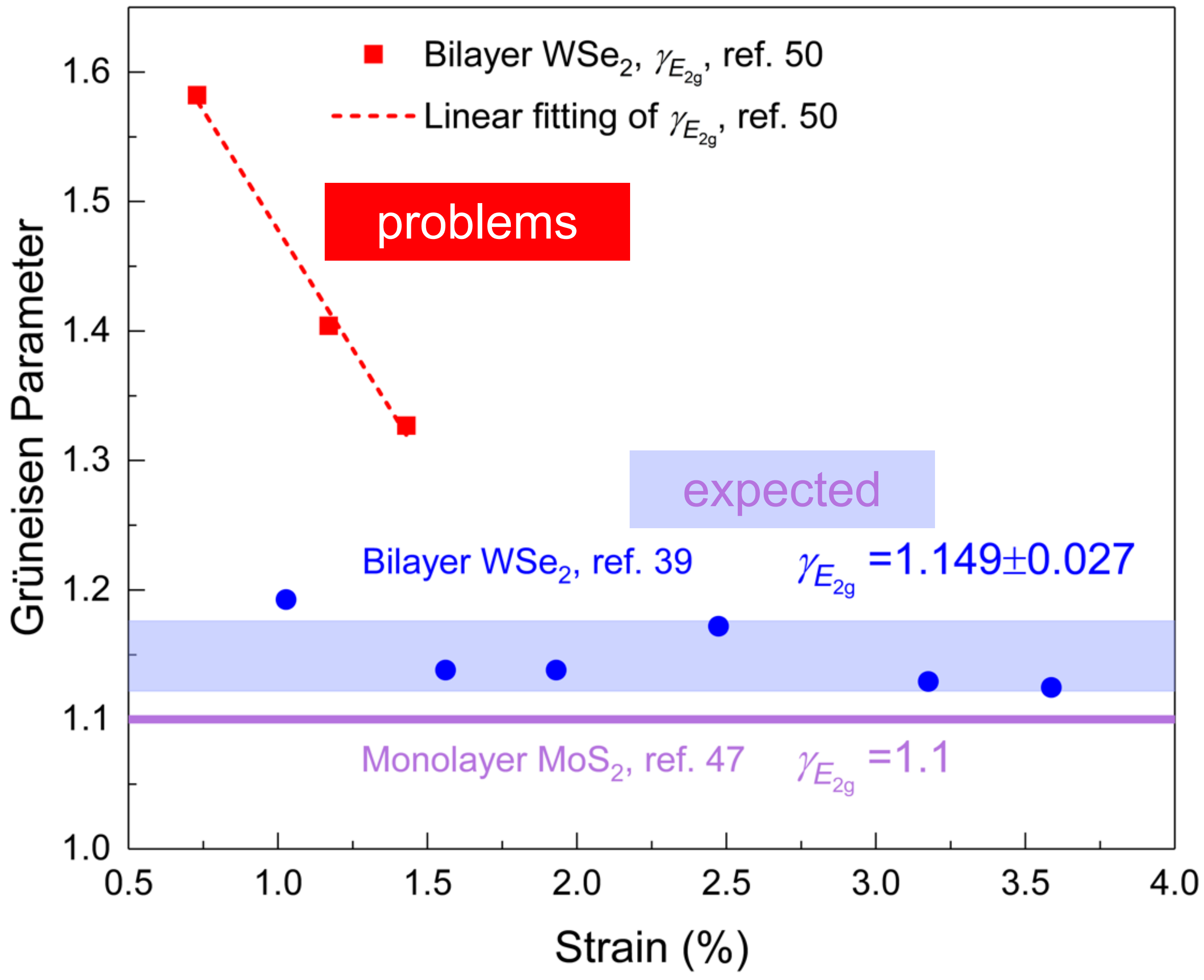


Now for our bilayer WSe_2

Measured Grüneisen parameter of bi-layer WSe_2



Calibration/validation is critically important

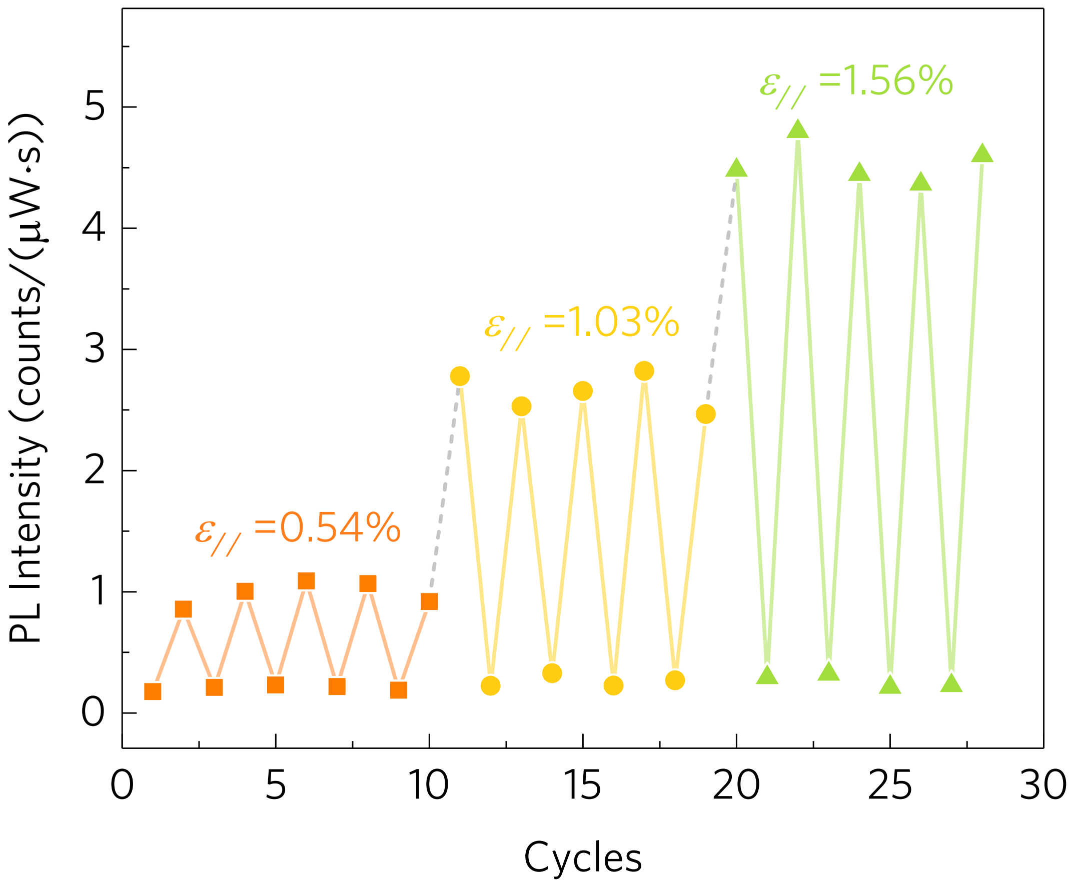


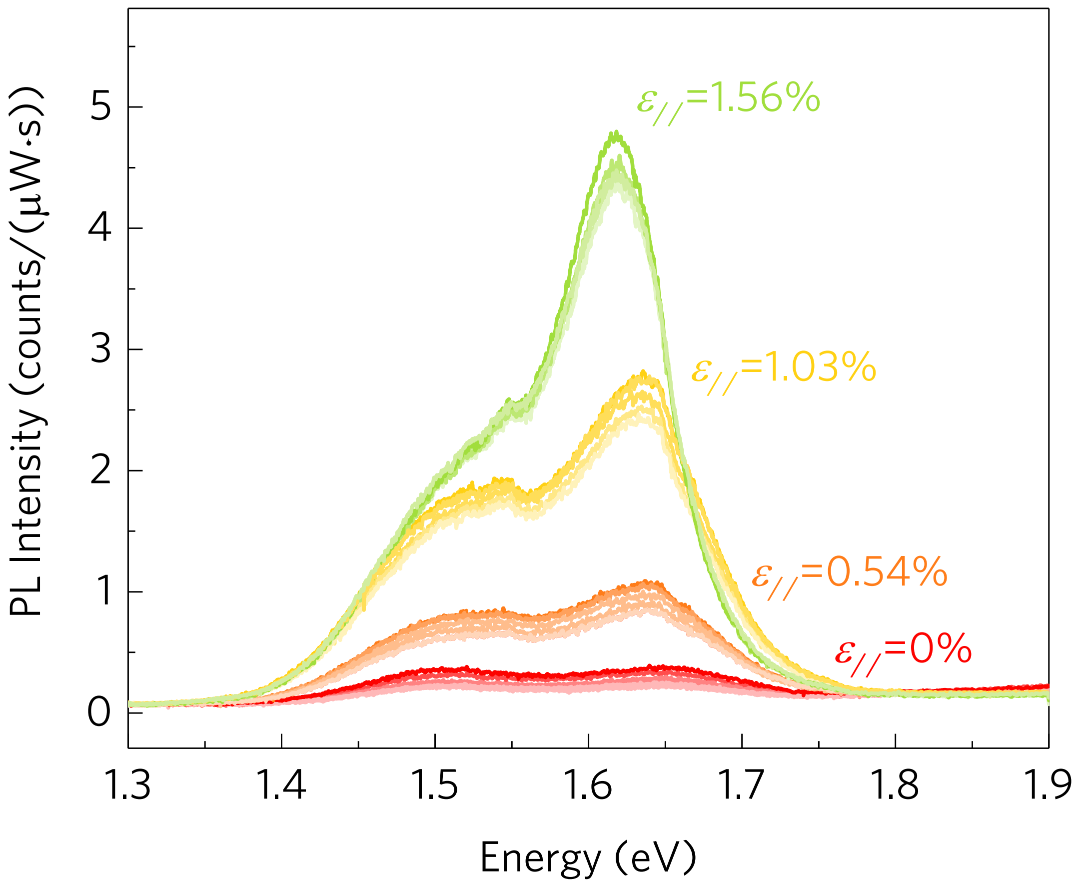
39. Wu, W., Wang, J., Ercius, P., Wright, N. C., Leppert-Simenauer, D. M., Burke, R. A., Dubey, M., Dogare, A. M., & Pettes, M. T. Giant mechano-optoelectronic effect in an atomically thin semiconductor. *Nano Letters* **18**, 2351-2357 (2018). http://dx.doi.org/10.1021/acs.nanolett.7b05229

47. Conley, H. J., Wang, B., Ziegler, J. I., Haglund, R. F., Jr., Pantelides, S. T., & Bolotin, K. I. Bandgap engineering of strained monolayer and bilayer MoS$_2$. *Nano Letters* **13**, 3626-3630 (2013). http://dx.doi.org/10.1021/nl4014748

50. Desai, S. B., Seol, G., Kang, J. S., Fang, H., Battaglia, C., Kapadia, R., Ager, J. W., Guo, J., & Javey, A. Strain-induced indirect to direct bandgap transition in multilayer WSe$_2$. *Nano Letters* **14**, 4592-4597 (2014). http://dx.doi.org/10.1021/nl501638a

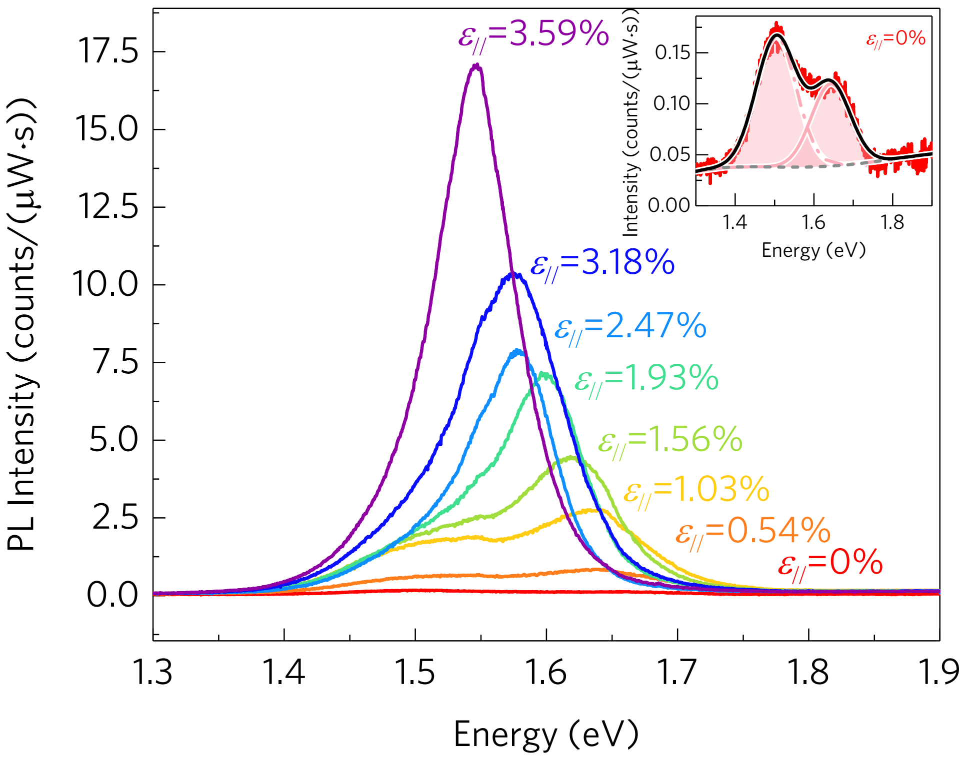
Cycling results indicate we remain in the elastic regime

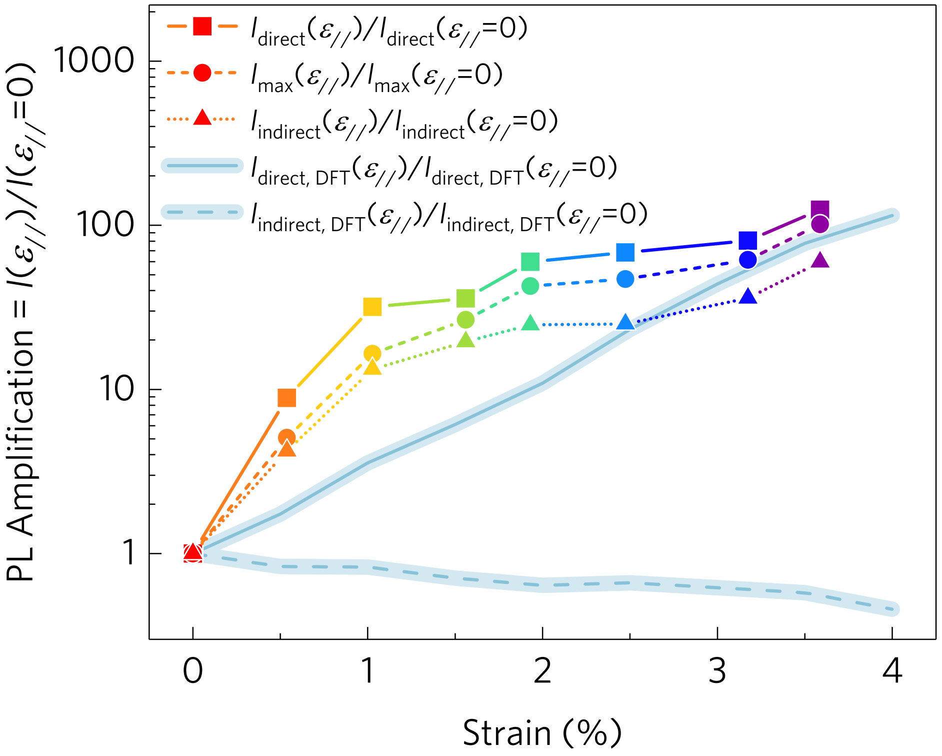




Amplification of the photoluminescence intensity

Maximum PL intensity is enhanced by ~101× at 3.6% strain
Maximum PL enhancement of A exciton is 124×

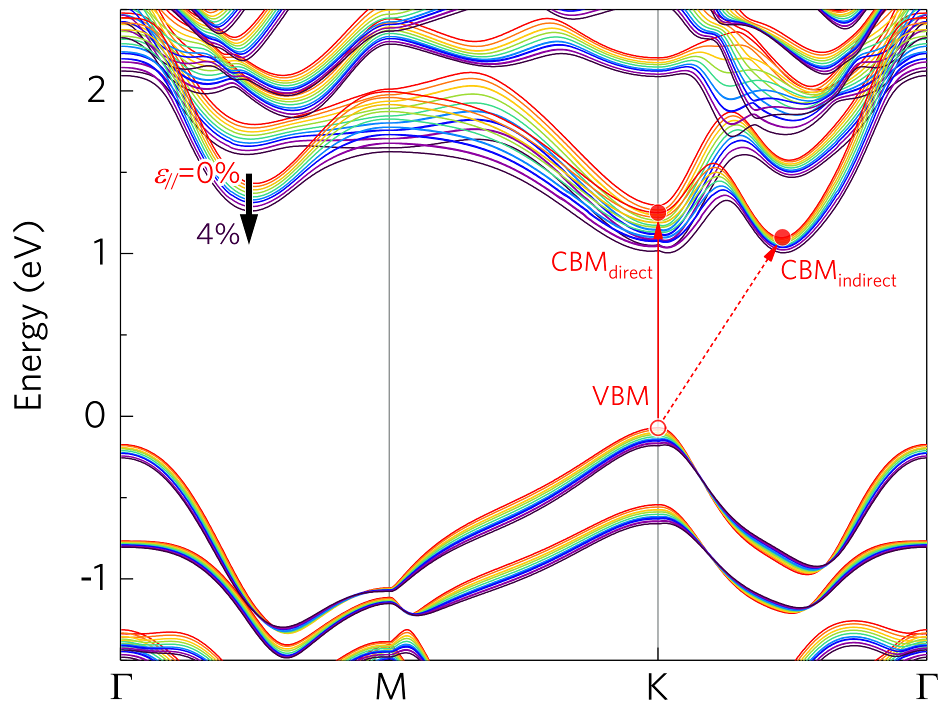


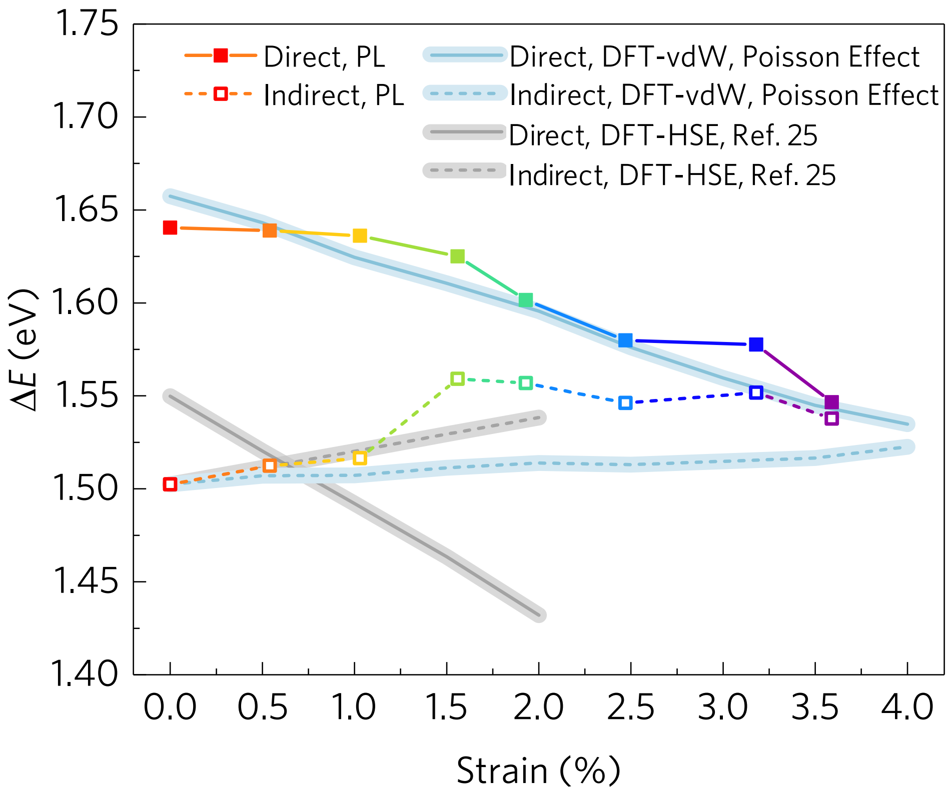


DFT by Jin Wang & Avinash Dongare, UConn MSE

Indirect-to-direct electronic band transition conversion

DFT theoretical prediction which includes realistic system conditions – van der Waals interaction and 3D Poisson effect – explains experimental observation





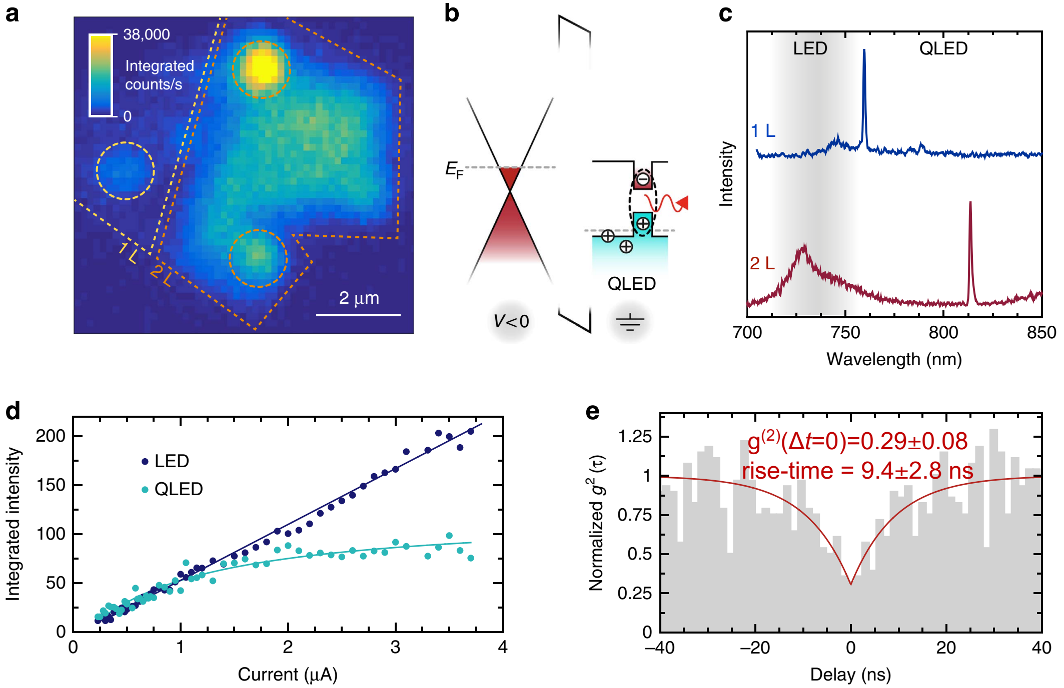
We have compared our results and DFT model with:

[25] S. B. Desai and A. Javey *et al.*, *Nano Lett.* **2014**, *14*, 4592. http://dx.doi.org/10.1021/nl501638a

Implications:
Strain Strongly Impacts Energy Landscape
– Quantum Emission from Locally Strained Epitaxial WSe_2 –

Motivation: Single photon sources

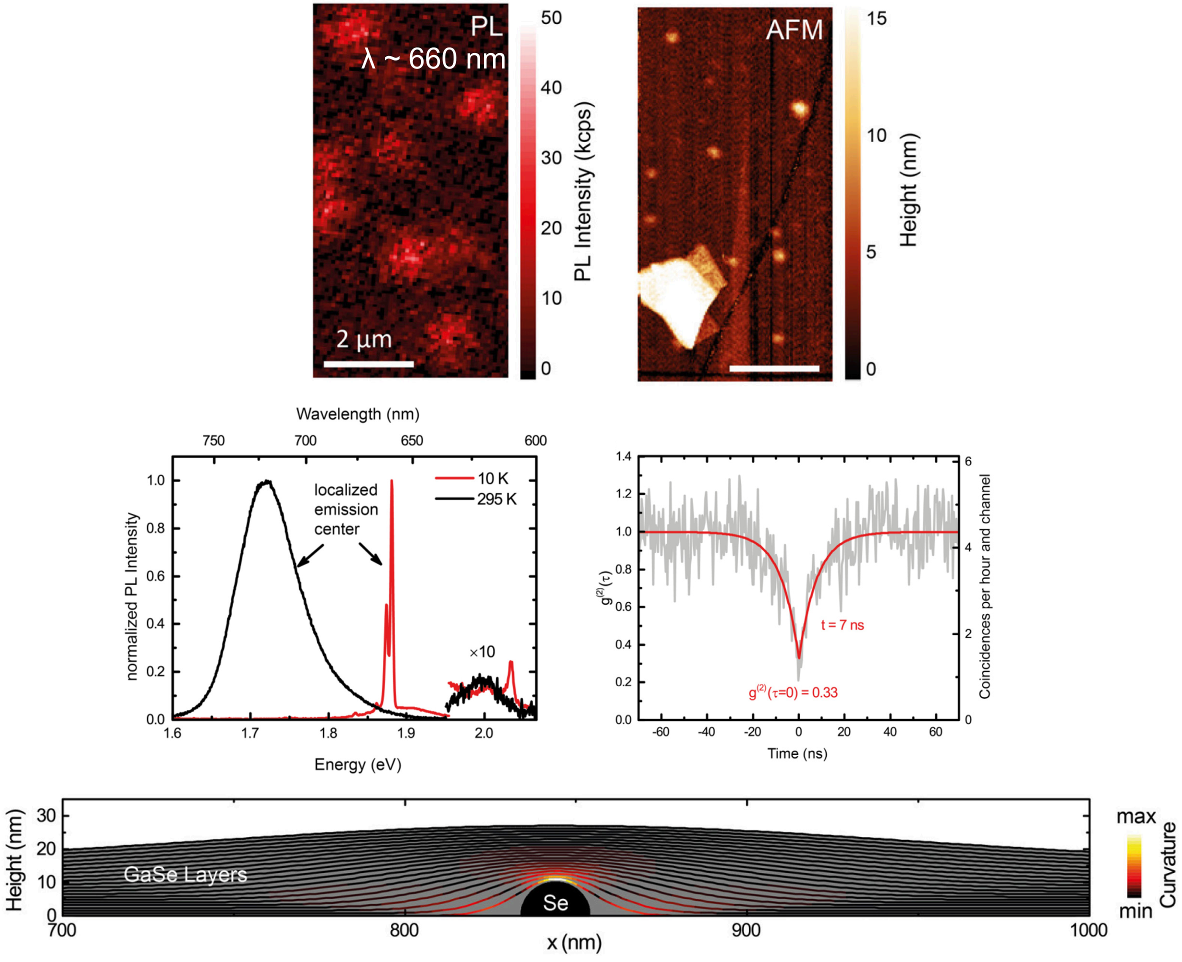
WSe_2: Electrically & Optically Driven



Palacios-Berraquero & Atatüre 2016, https://doi.org/10.1038/ncomms12978

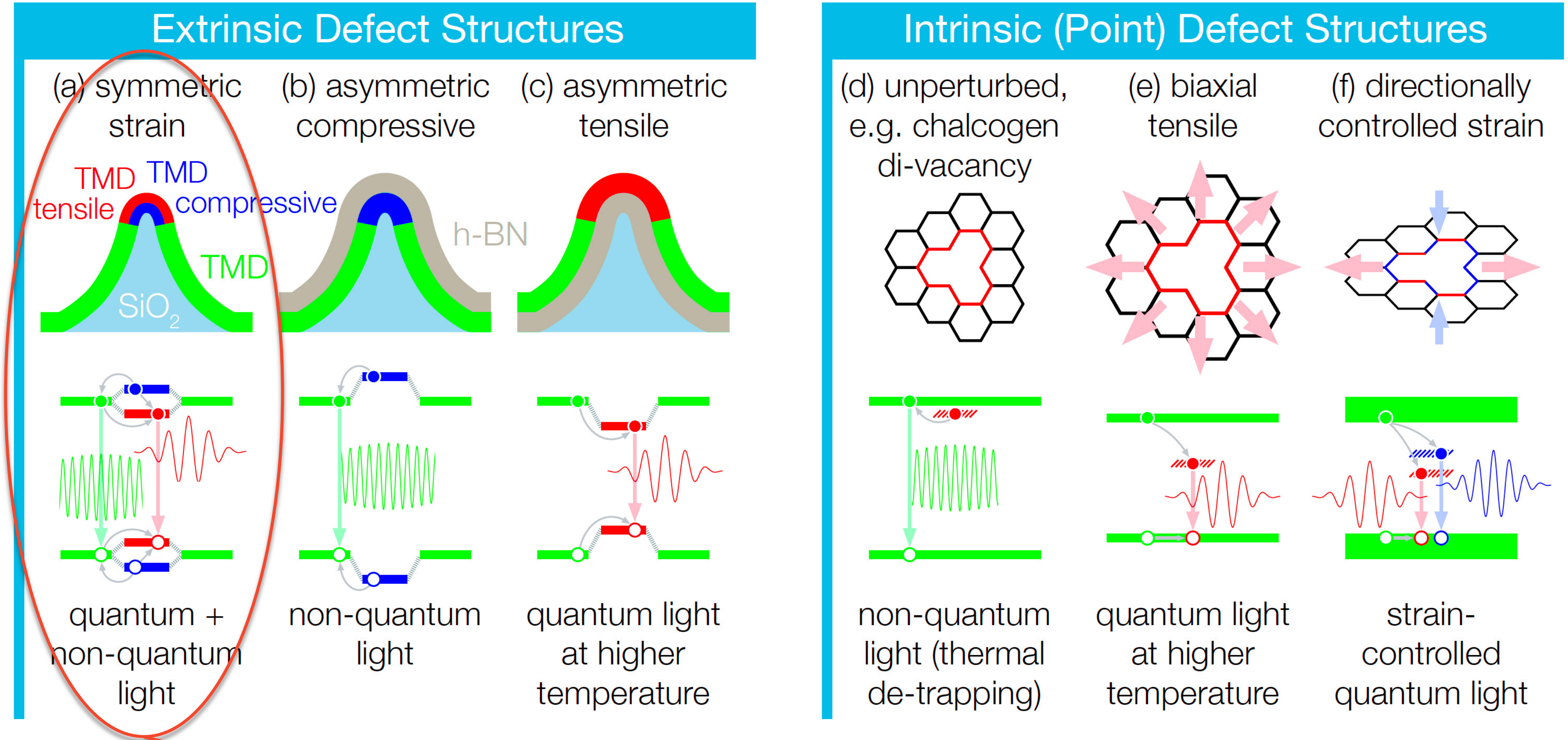
- *Method responsible for emission sites is hypothesized to be potential well-type energy band structure*
- *Other atomically-thin semiconducting materials are likely to yield similar results decorating different spectral windows*

GaSe: Optically Driven



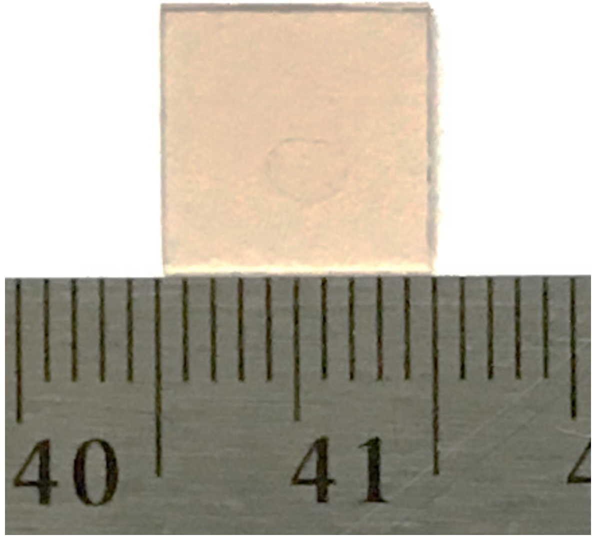
Tonndorf & Bratschitsch 2017, https://doi.org/10.1088/2053-1583/aa525b

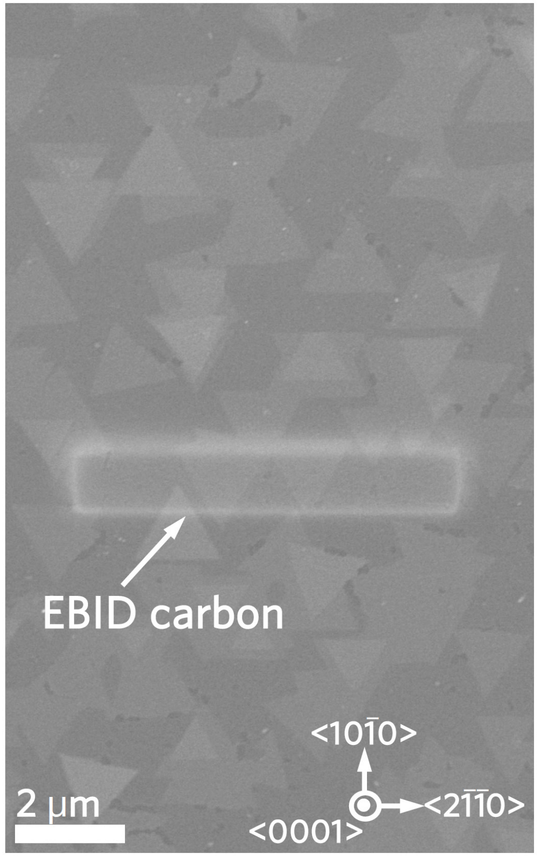
Hypotheses

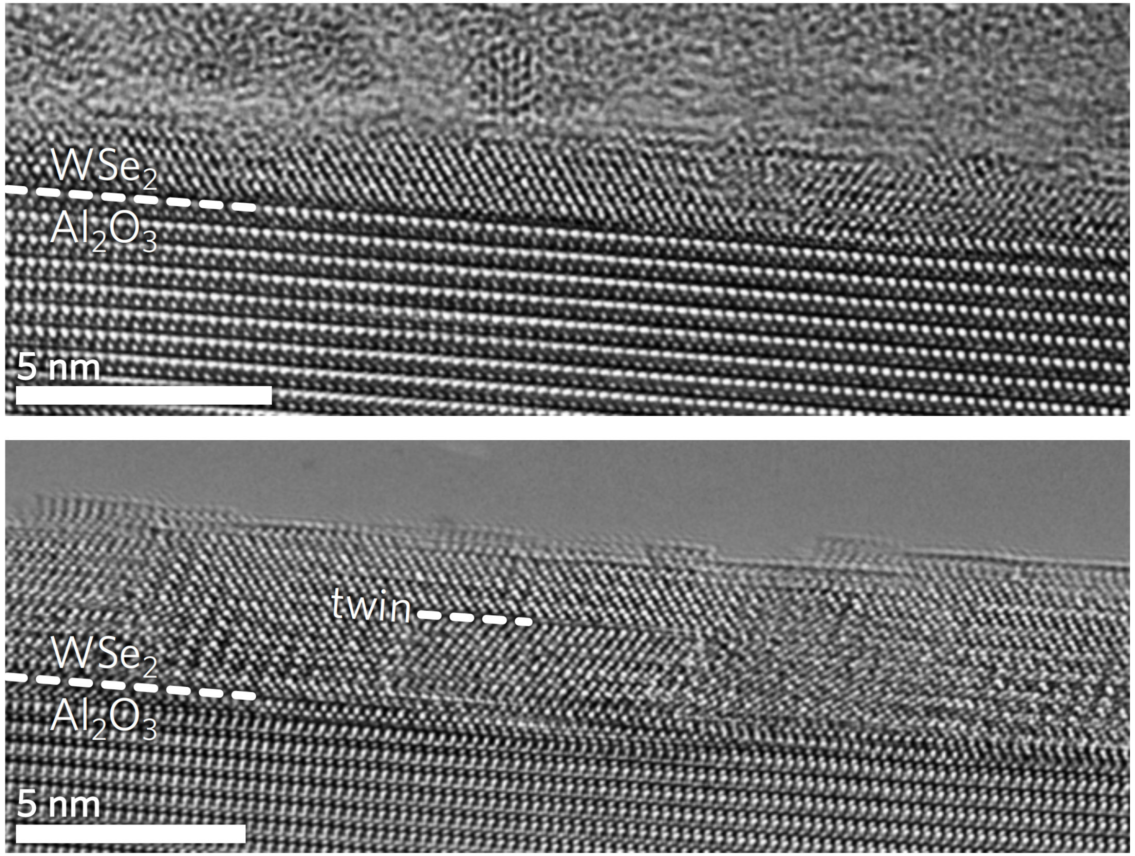


I will focus here in this presentation

Epitaxial WSe_2 synthesized by Joan Redwing's group



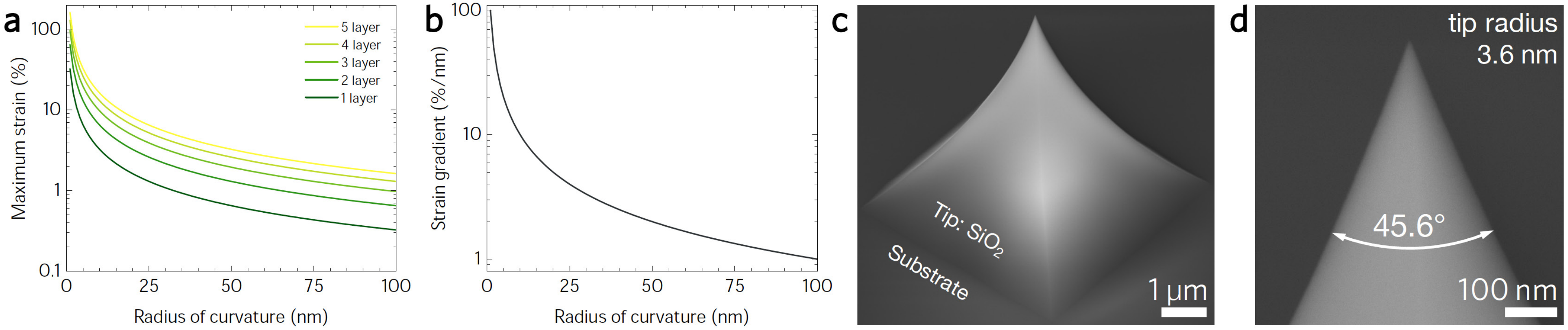




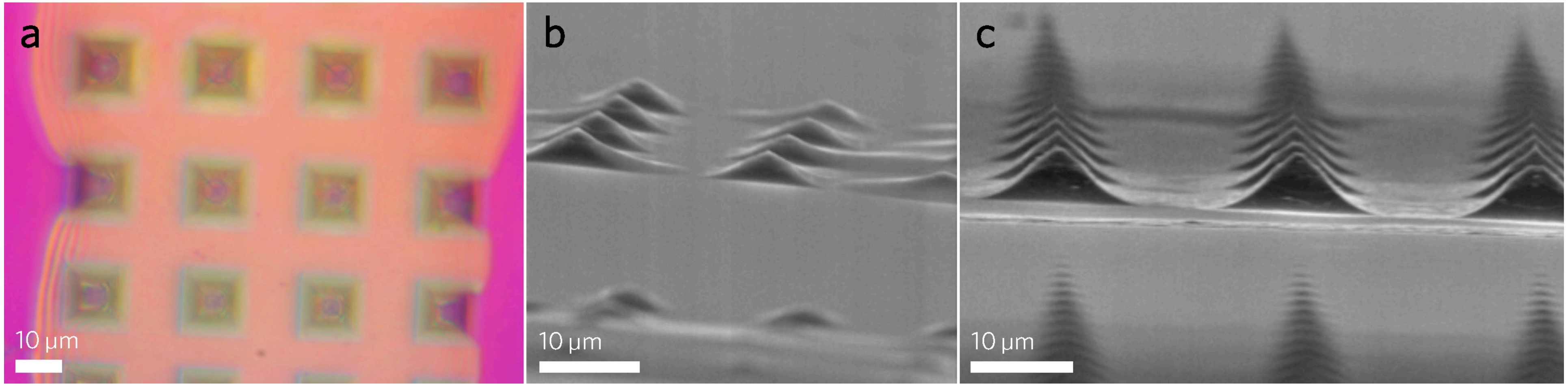
- vertical cold-wall CVD reaction scheme using $W(CO)_6$ and H_2Se
- grain size ~200-500 nm
- grown on 1 × 1 cm sapphire substrate
- current synthesis is uniform over a 2" diameter substrate

Ultra-sharp tip arrays force recombination through highly localized strain

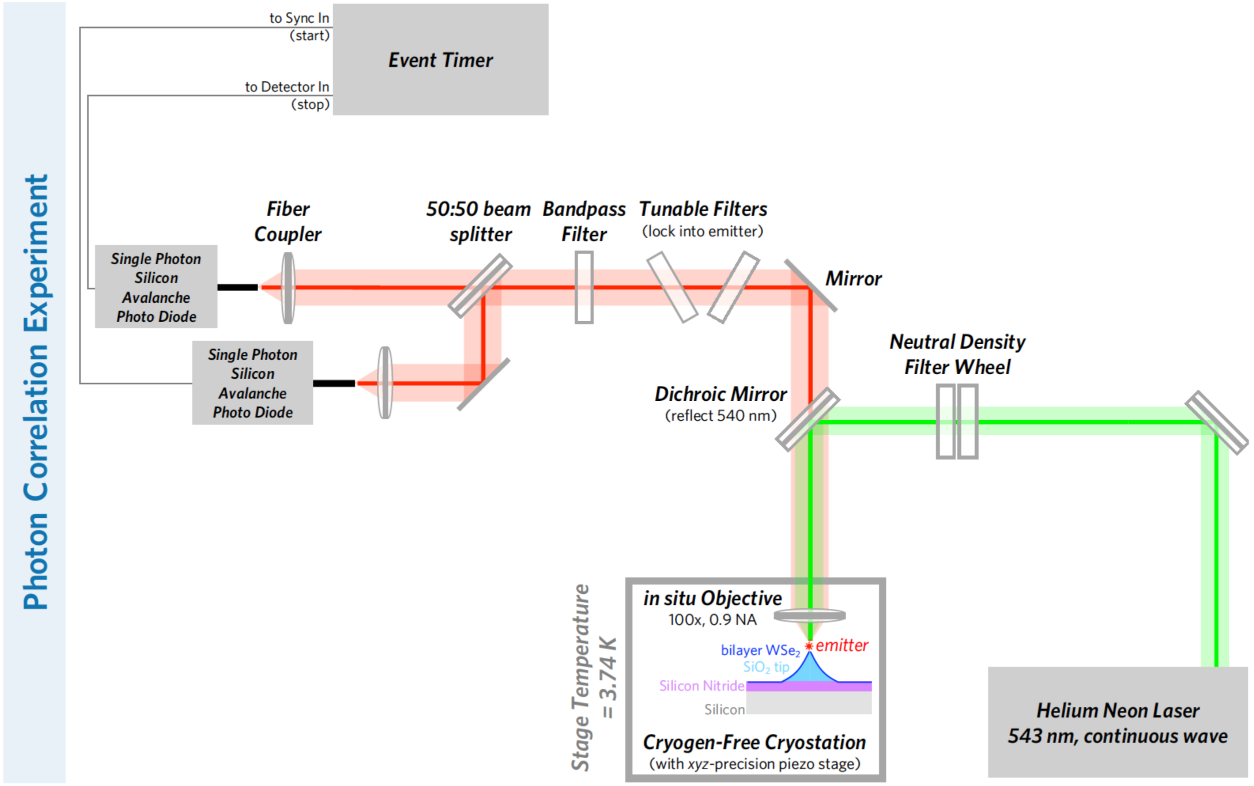
Large strain and strain gradients are possible for atomically-thin crystals transferred onto ultra-sharp tips

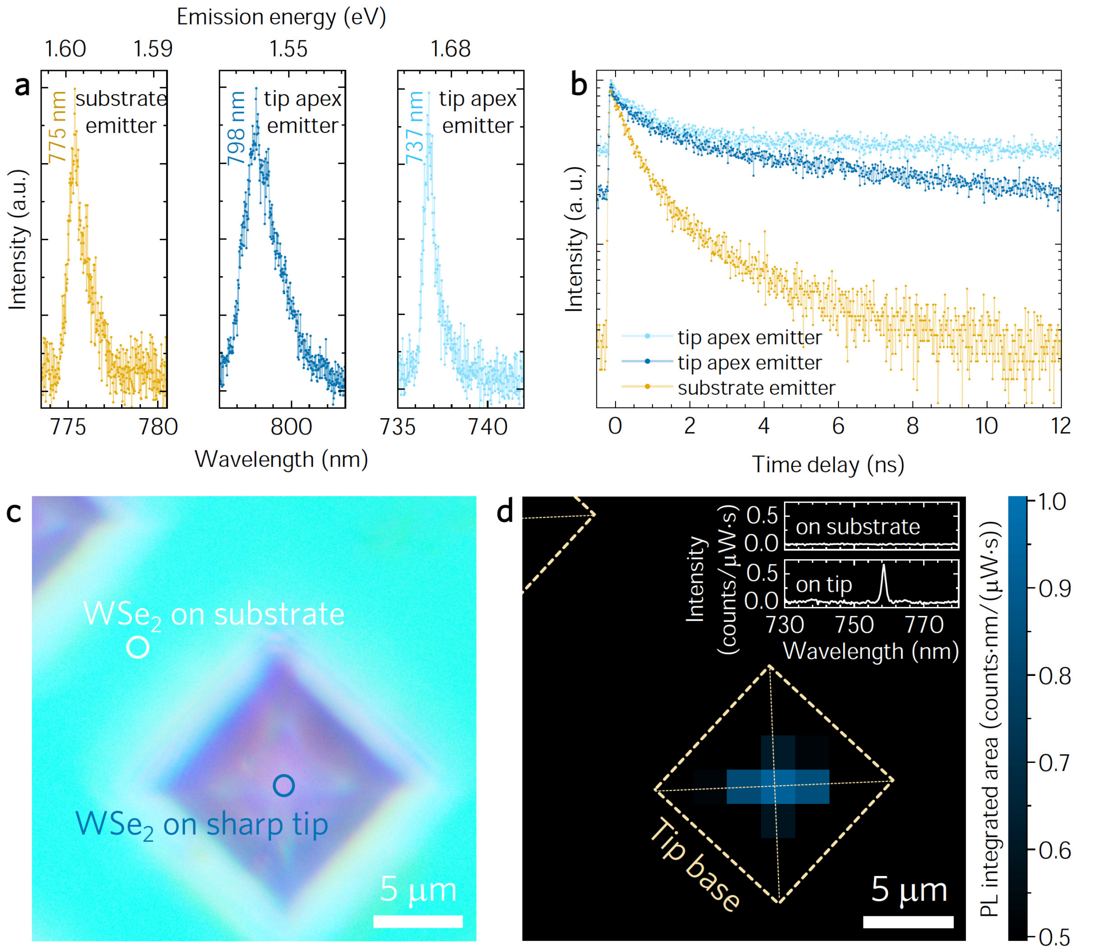


Puncture-free transfer onto ultra-sharp tip array

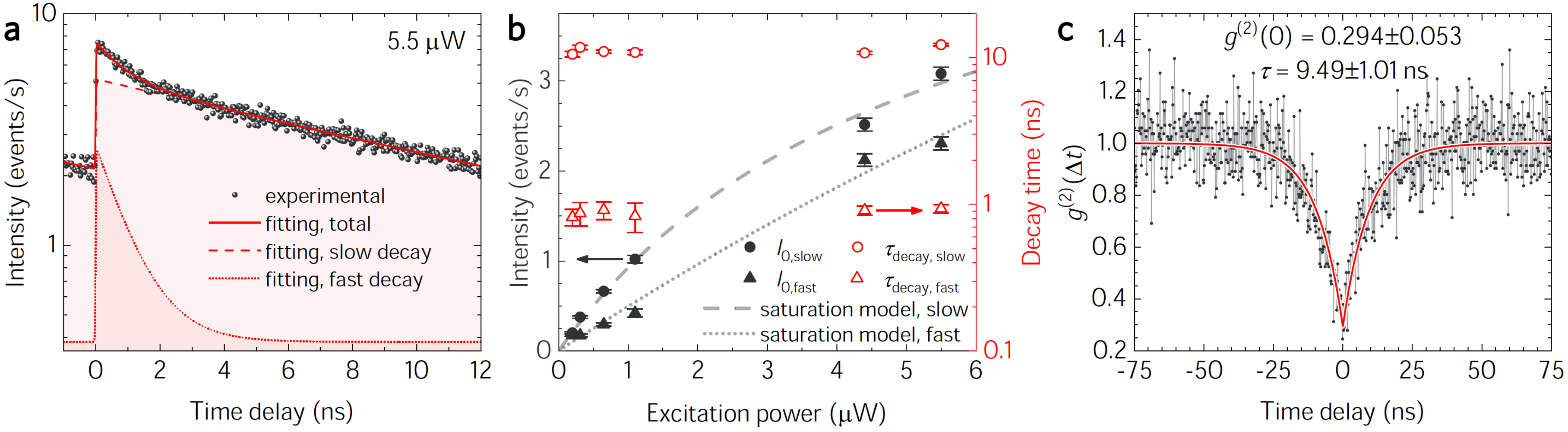


Beam path for optical experiments (PL, TRPL, and Hanbury-Brown-Twiss interferometry)





Exciton dynamics of emission



TRPL:

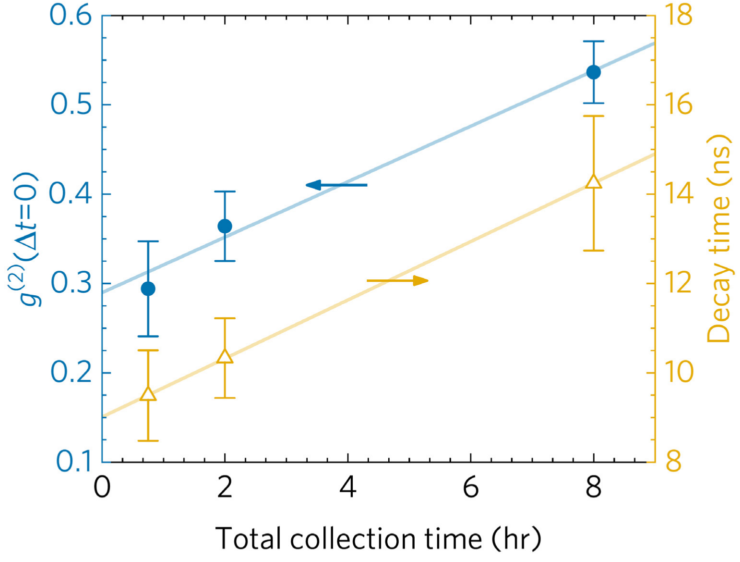
fast decay 0.80±0.04 ns

slow decay 11.20±0.66 ns

HBT:

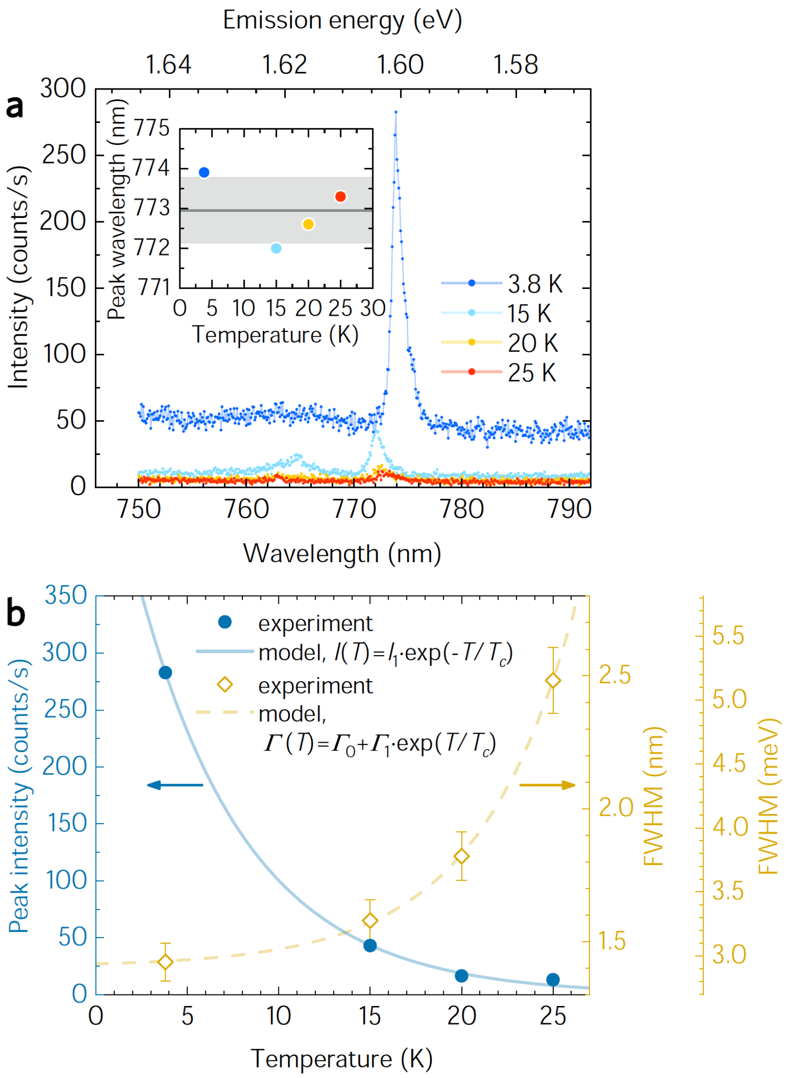
intrinsic $g^{(2)}(\Delta t=0)$ = 0.284±0.062

intrinsic τ_{decay} = 9.01±1.56 ns



Photon field intensity correlation proves spatially-localized quantum emission at the apex of the ultra-sharp SiO_2 tip

Temperature dependence of emission



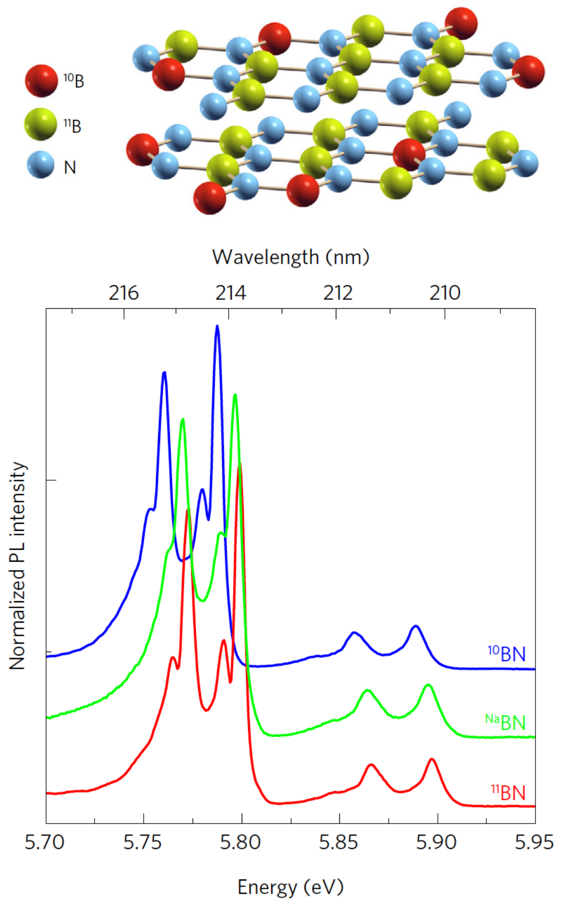
Low characteristic temperatures are a limiting feature of work in this field, generally < 10 K

Additional work needed to understand and increase thermal de-trapping energy, hence the new studies depicted in overview slide which will benefit from new 2DCC synthesis breakthroughs

Isotope Effect in Bi-layer WSe_2

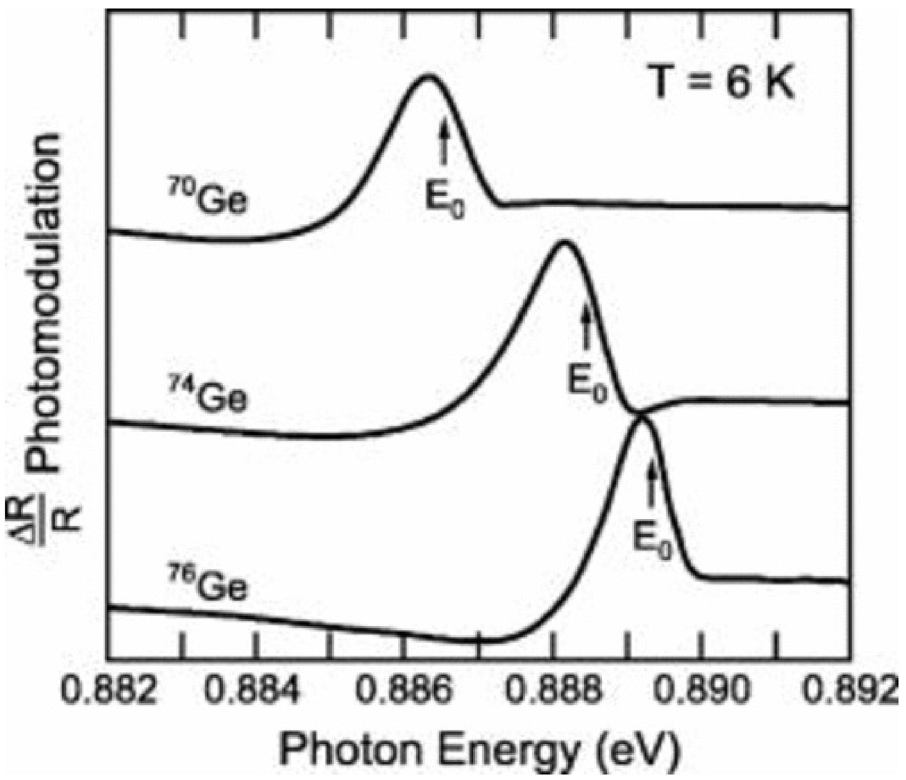
Surprising isotope effects on electronic structure in indirect band gap materials

Bulk Boron Nitride



Vuong & Cassabois 2018, https://doi.org/10.1038/nmat5048

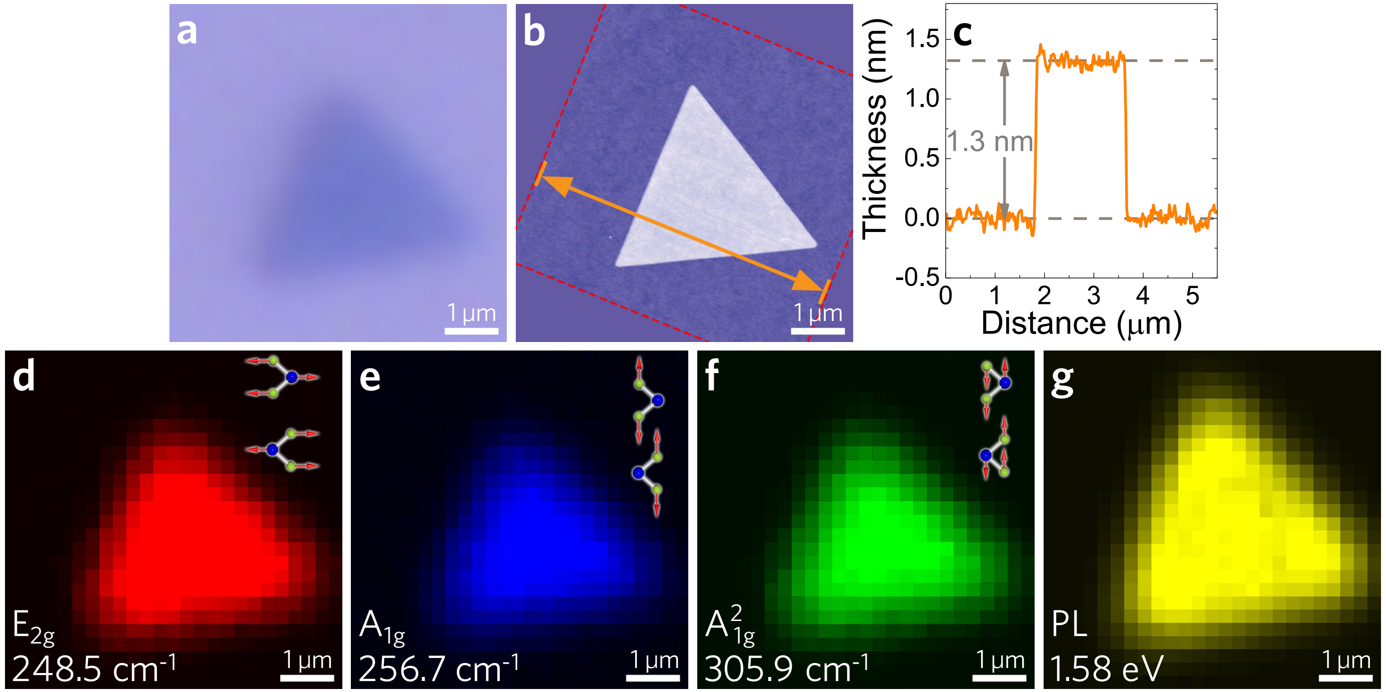
Also observed in bulk materials, e.g. Ge



Cardona & Thewalt 2005, https://doi.org/10.1103/RevModPhys.77.1173

Growth of $^{NA}W^{NA}Se_2$ and purified $^{186}W^{80}Se_2$

$^{186}W^{80}Se_2$ AFM, Raman, PL

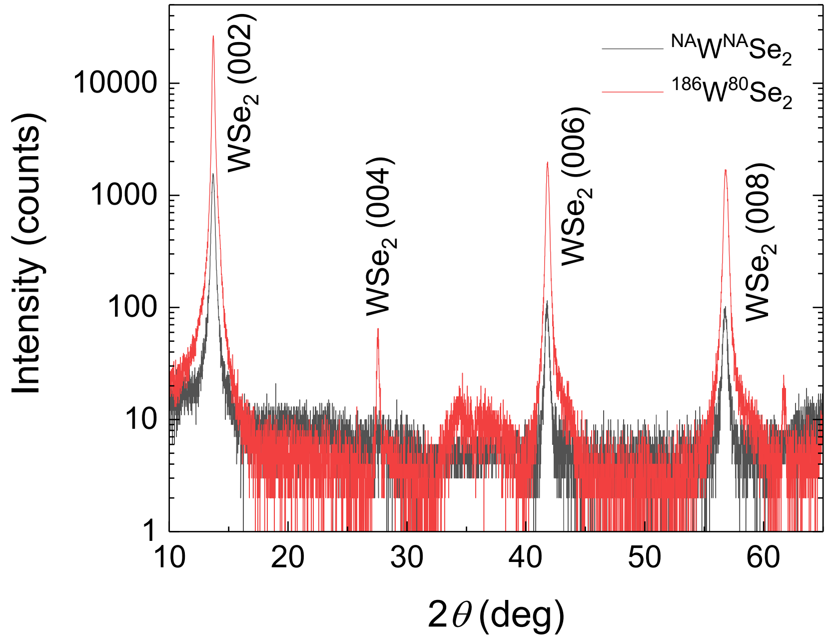


RBS stoichiometry, WSe_{2-x}

NA: x = 0.019±0.021

IE: x = -0.033±0.071

X-ray Diffraction

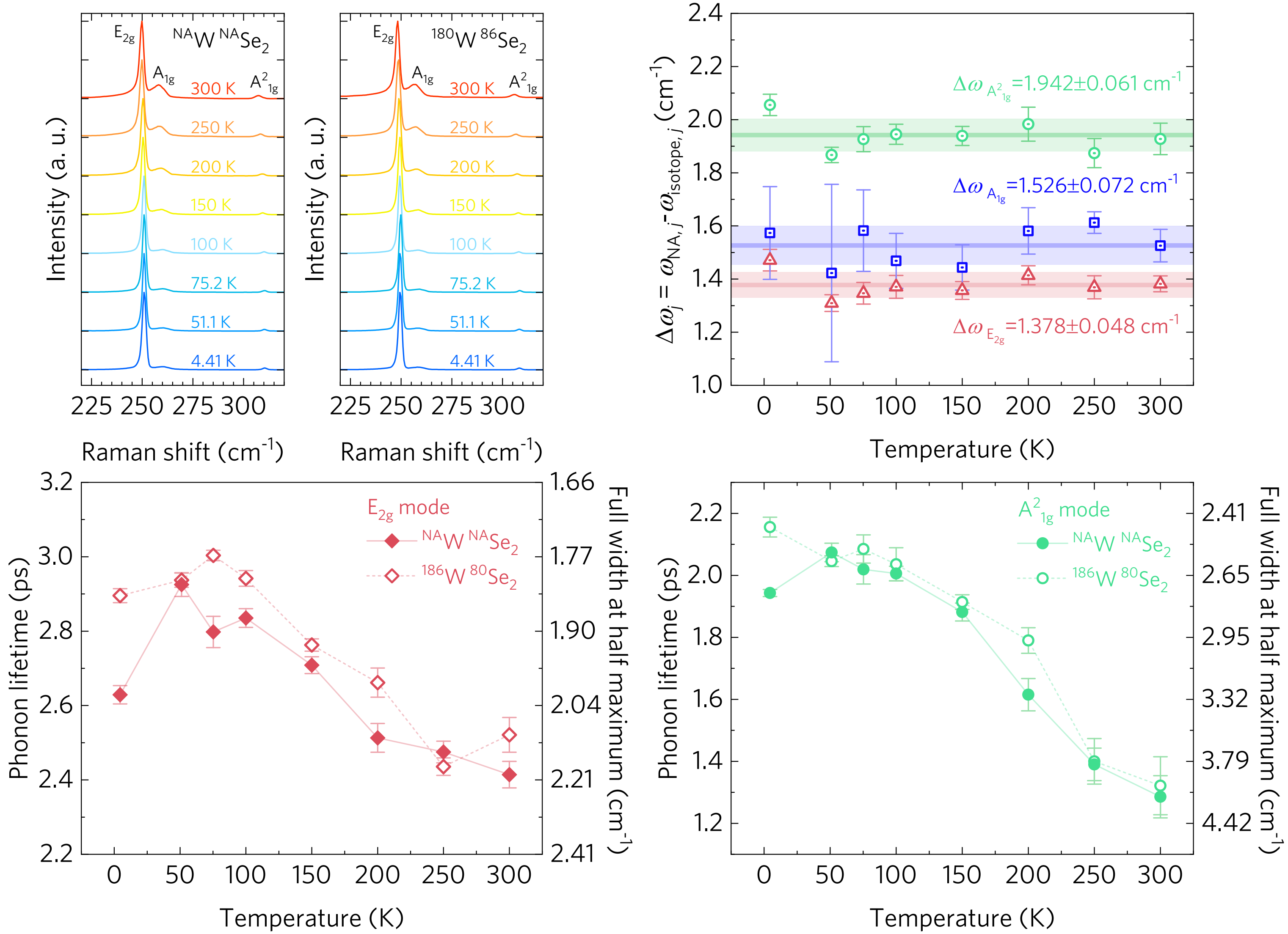


XRD w/ Rietveld refinement

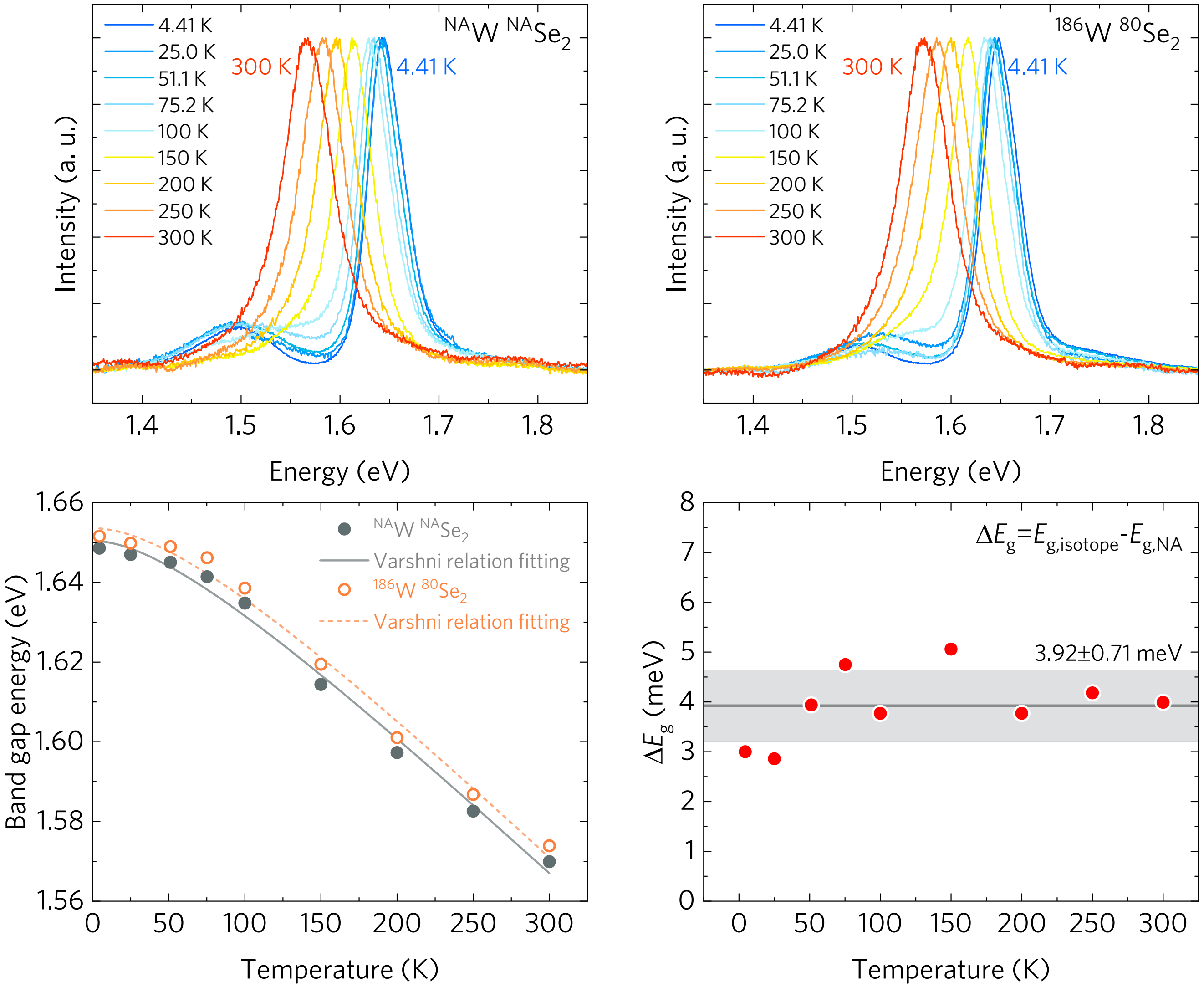
NA: 6.4670±0.0032 Å

IE: 6.4646±0.0007 Å

Vibrational spectra



Photoluminescence



PL blue-shift with increasing mass results from:

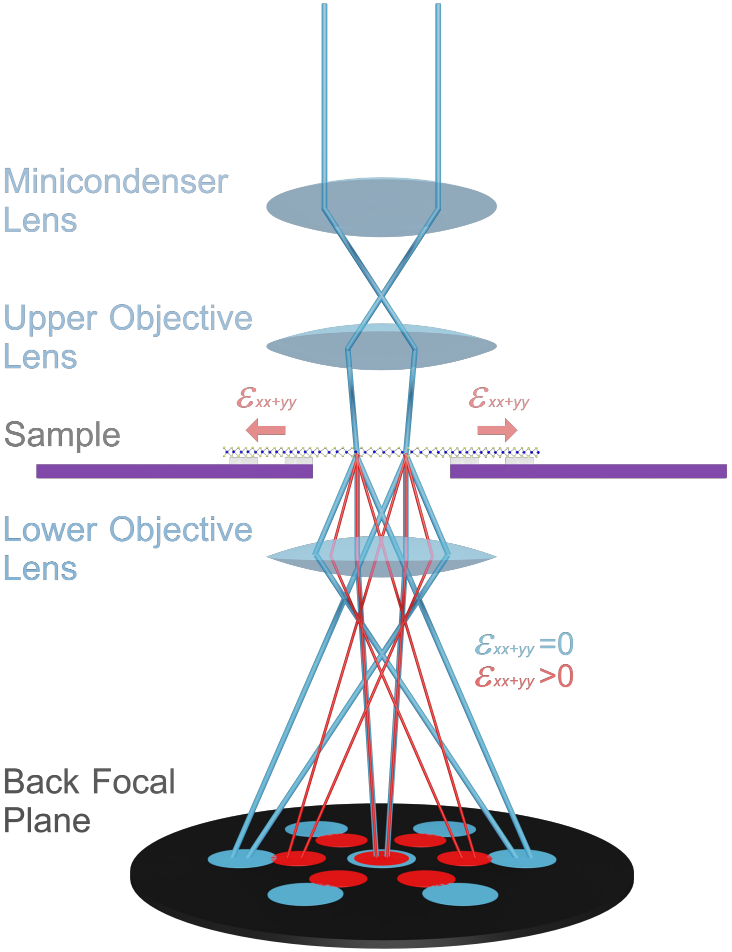
1. Isotopic shift towards lower phonon energy
2. Isotopic shift towards higher band-gap renormalization energy

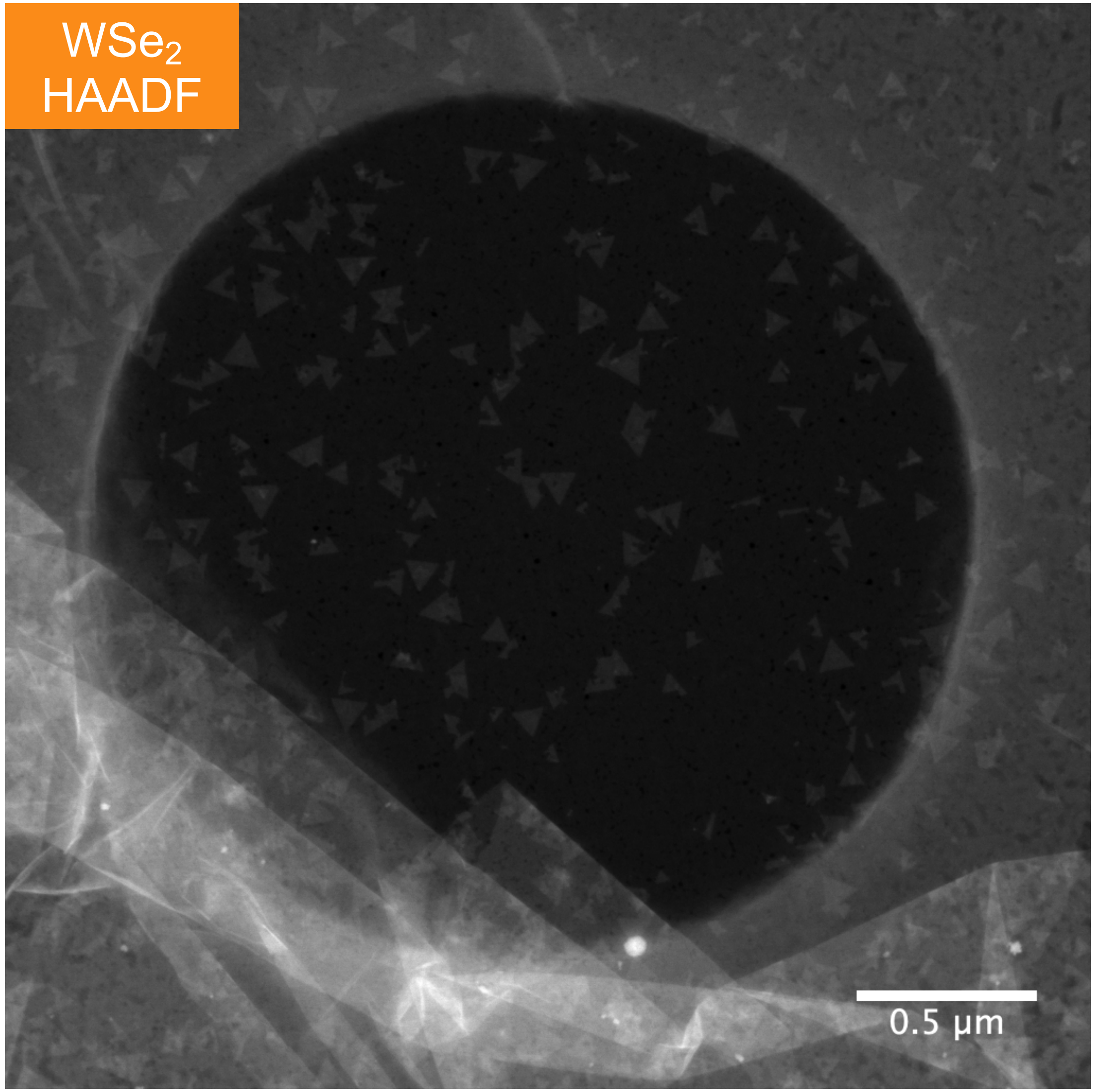
Need theoretical treatment to determine contributions to observed behavior, although our measurement leads us to postulate 2 dominates.

Local measurement of lattice parameters
4D Scanning Transmission Electron Microscopy

Understanding thermodynamic properties and strain profiles requires new approaches in nanometrology

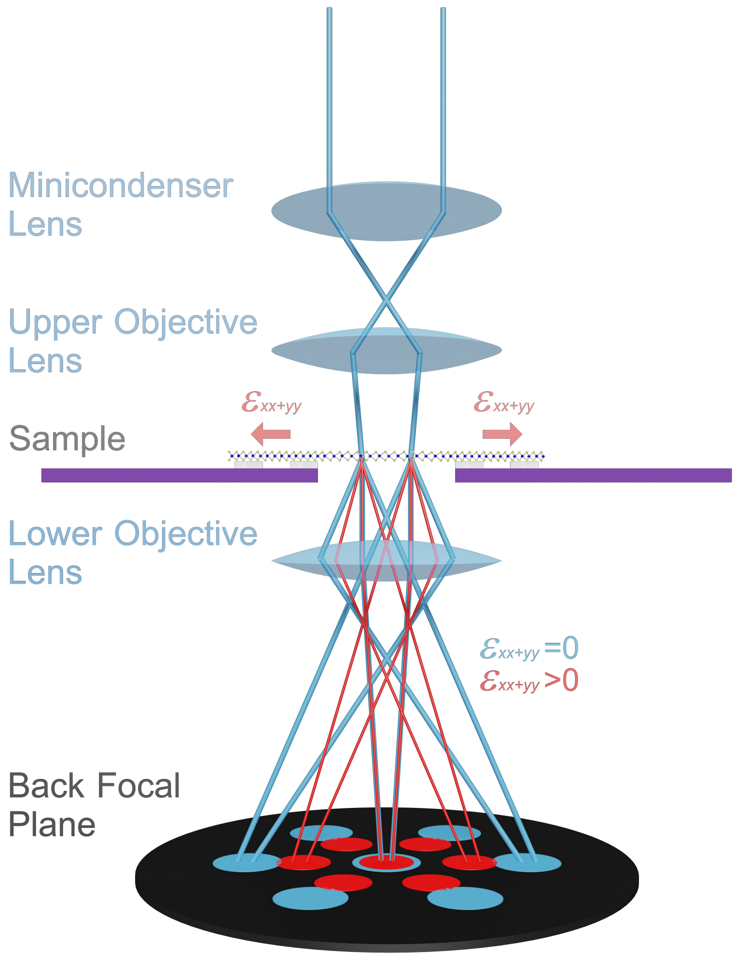
Schematic of Scanning Nanobeam Electron Diffraction of MOCVD WSe_2

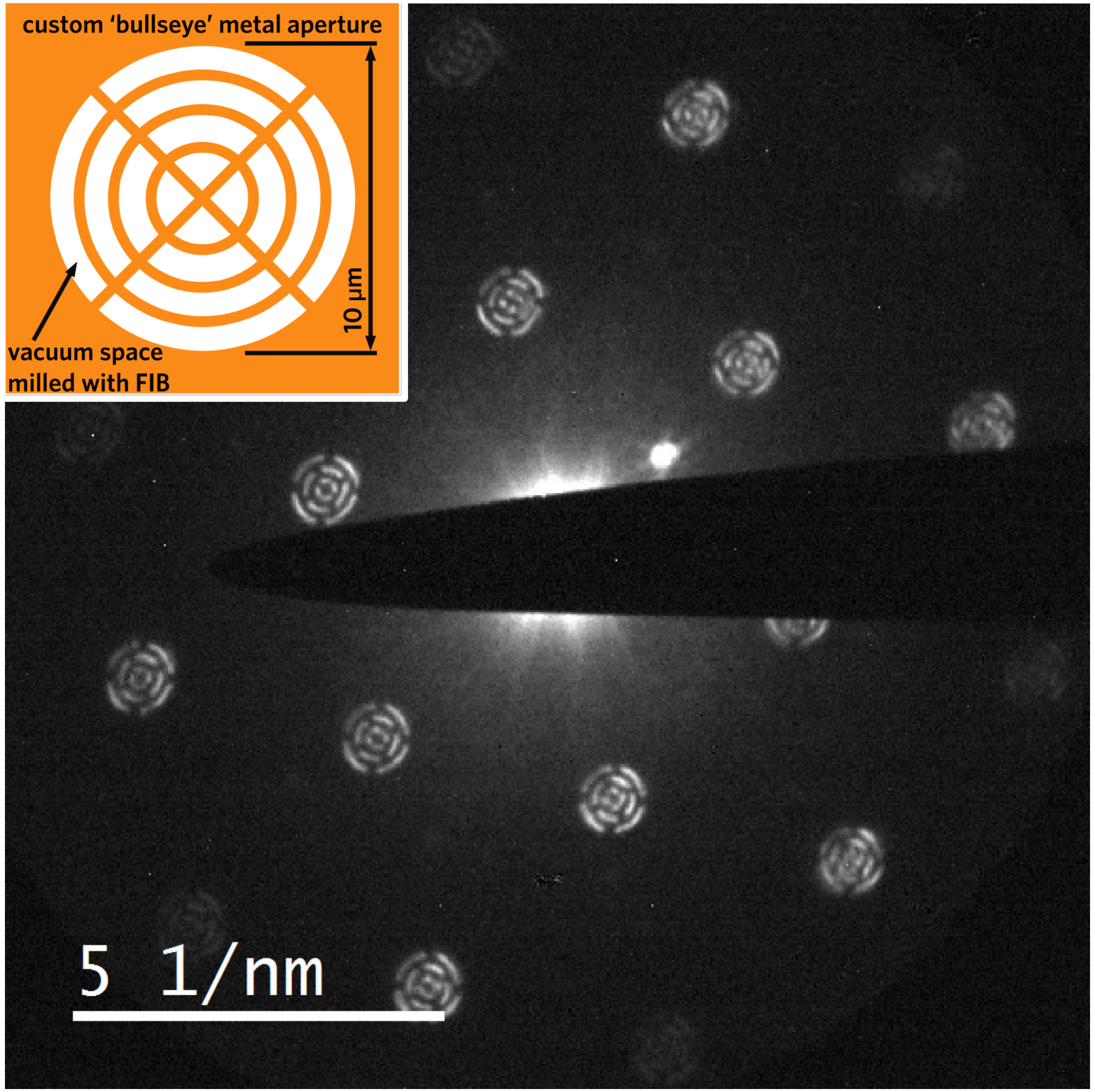




Probes can be patterned to increase number of features

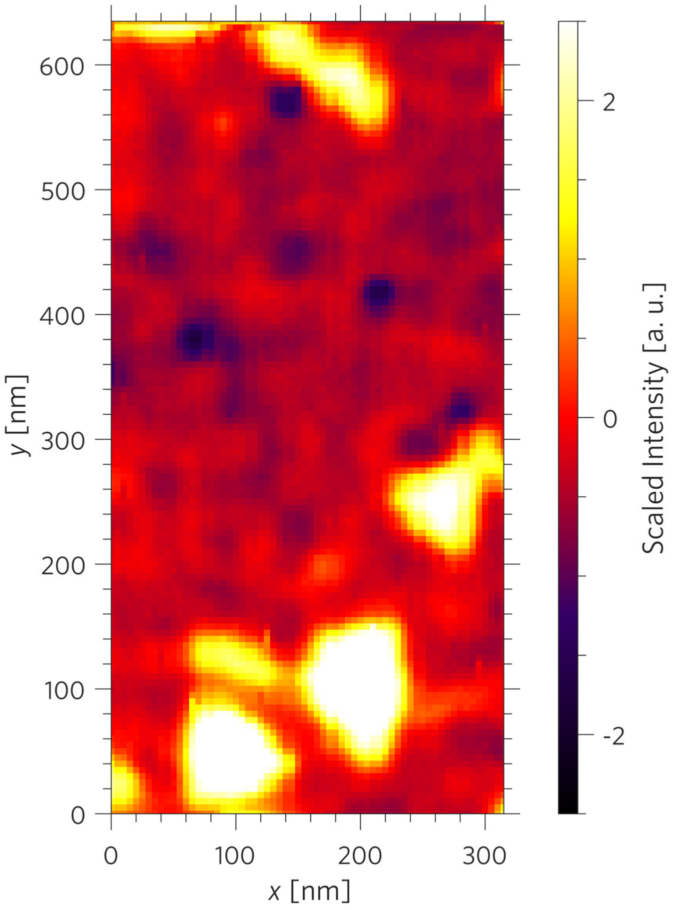
Schematic of scanning nanobeam electron diffraction of MOCVD WSe_2



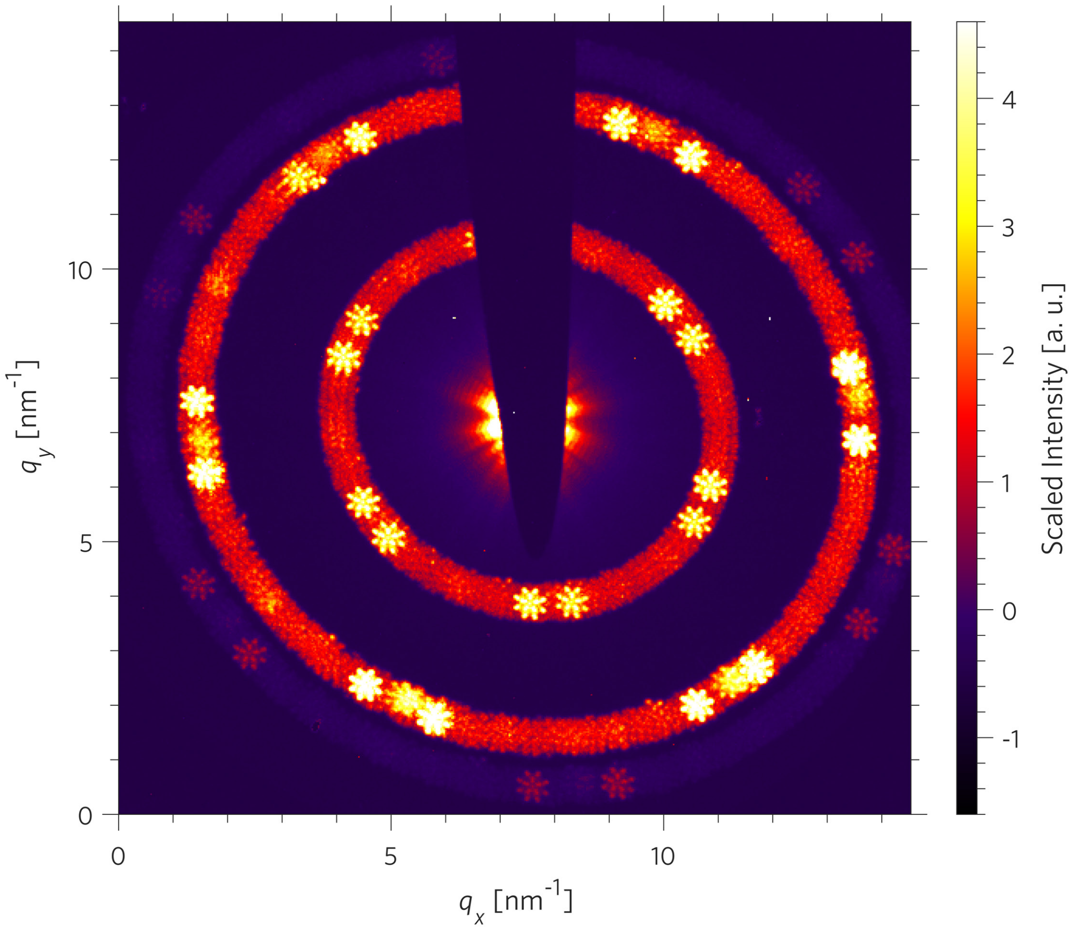


Nano beam electron diffraction

‘Virtual’ Bright Field



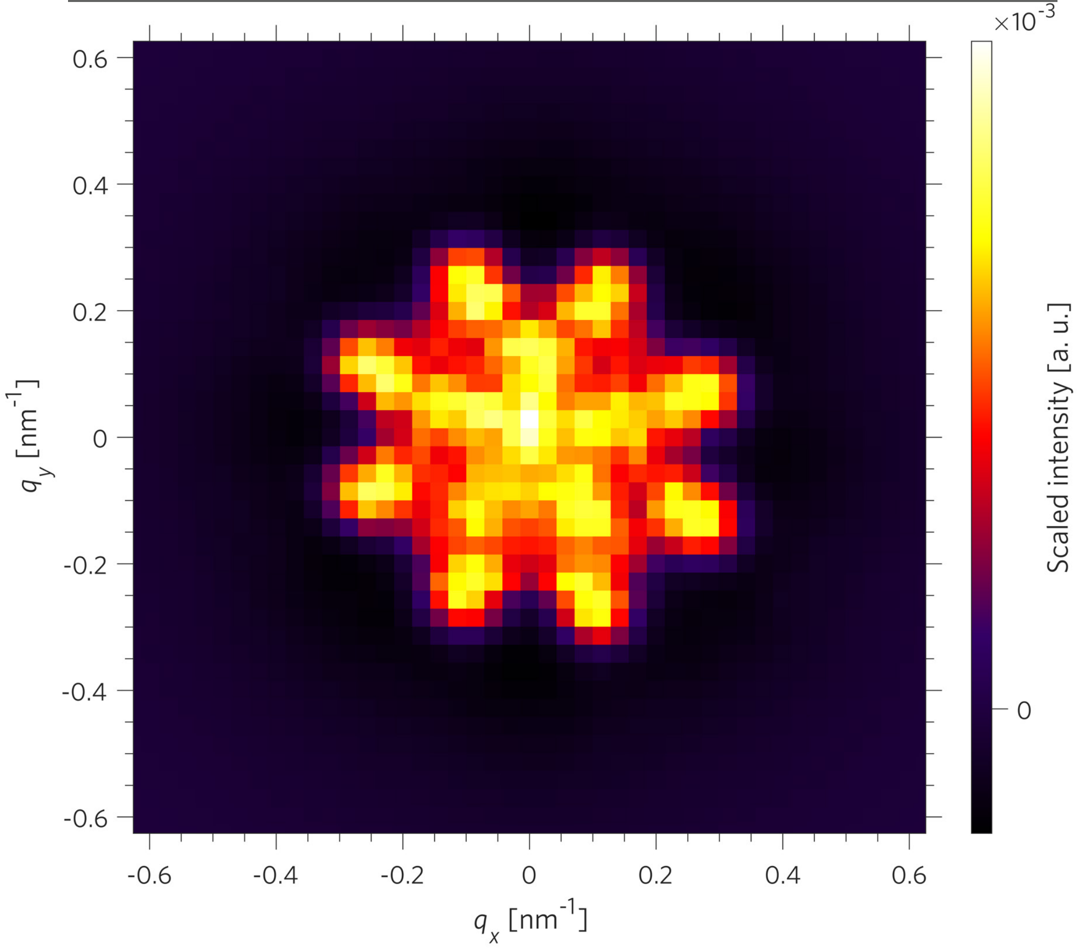
Maximum Intensity CBED Image 128 x 64



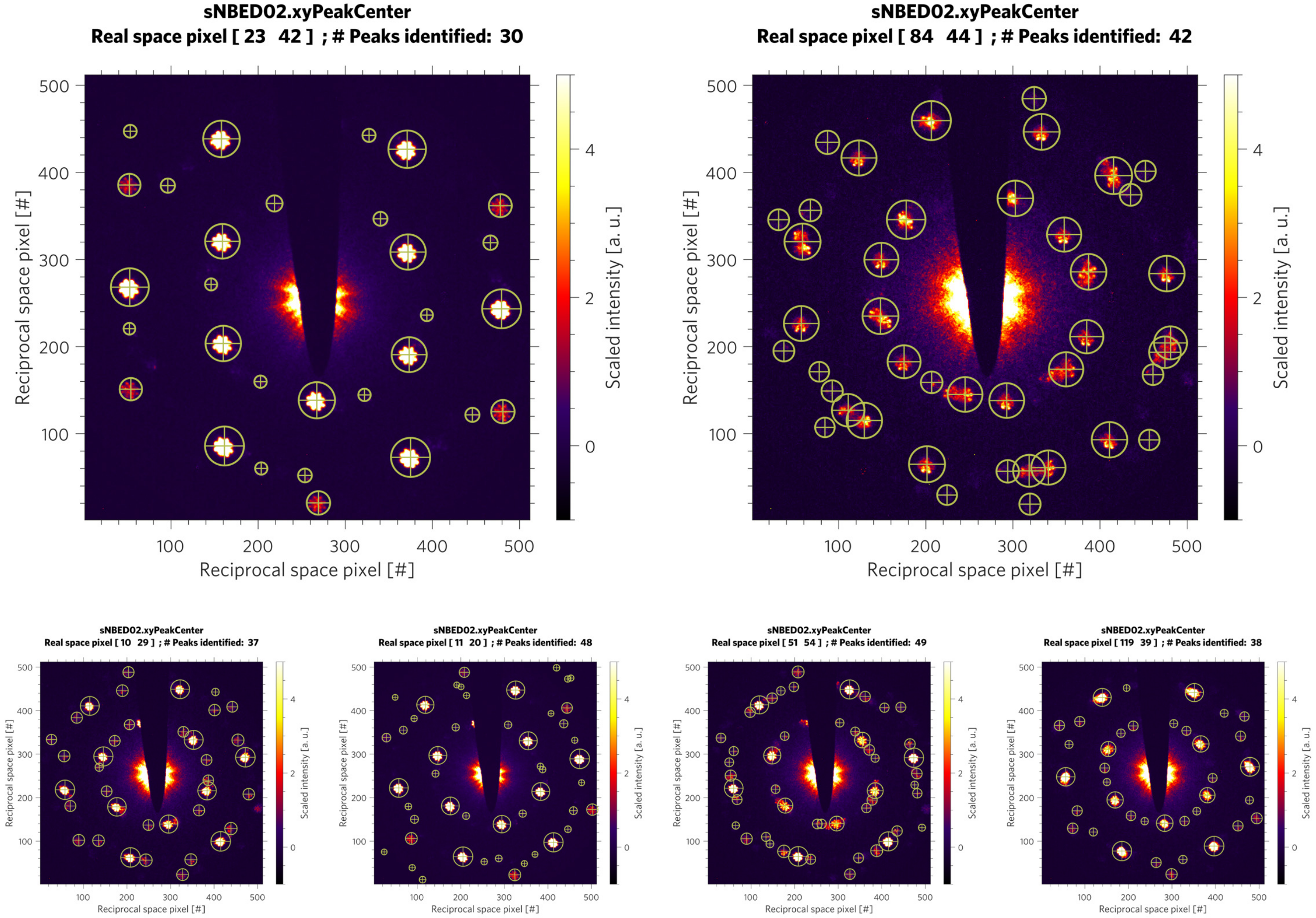
clear dominance of 12.5° grain boundaries

Nano beam electron diffraction

(000) Center Beam

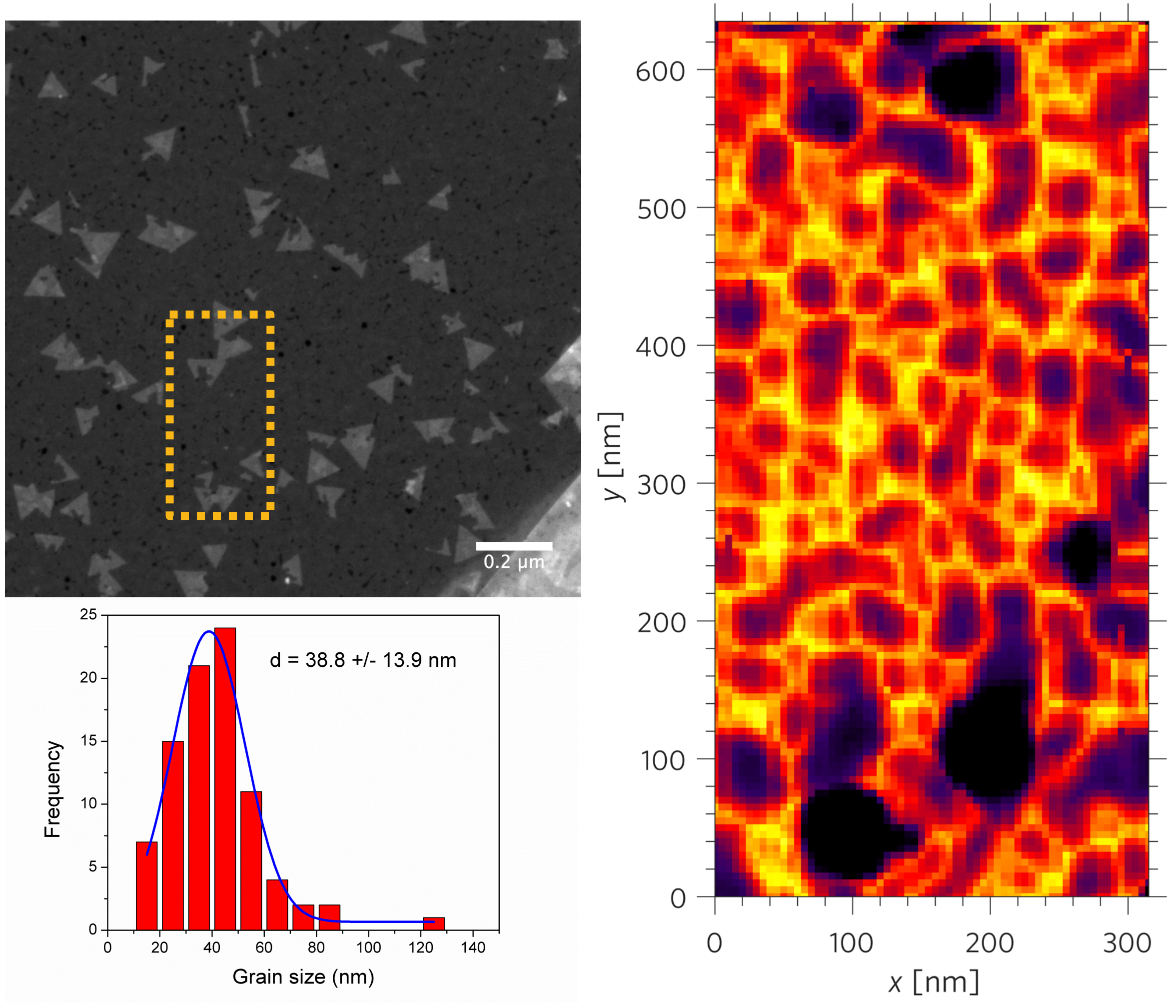


Cross Correlation to Locate Peak Centers

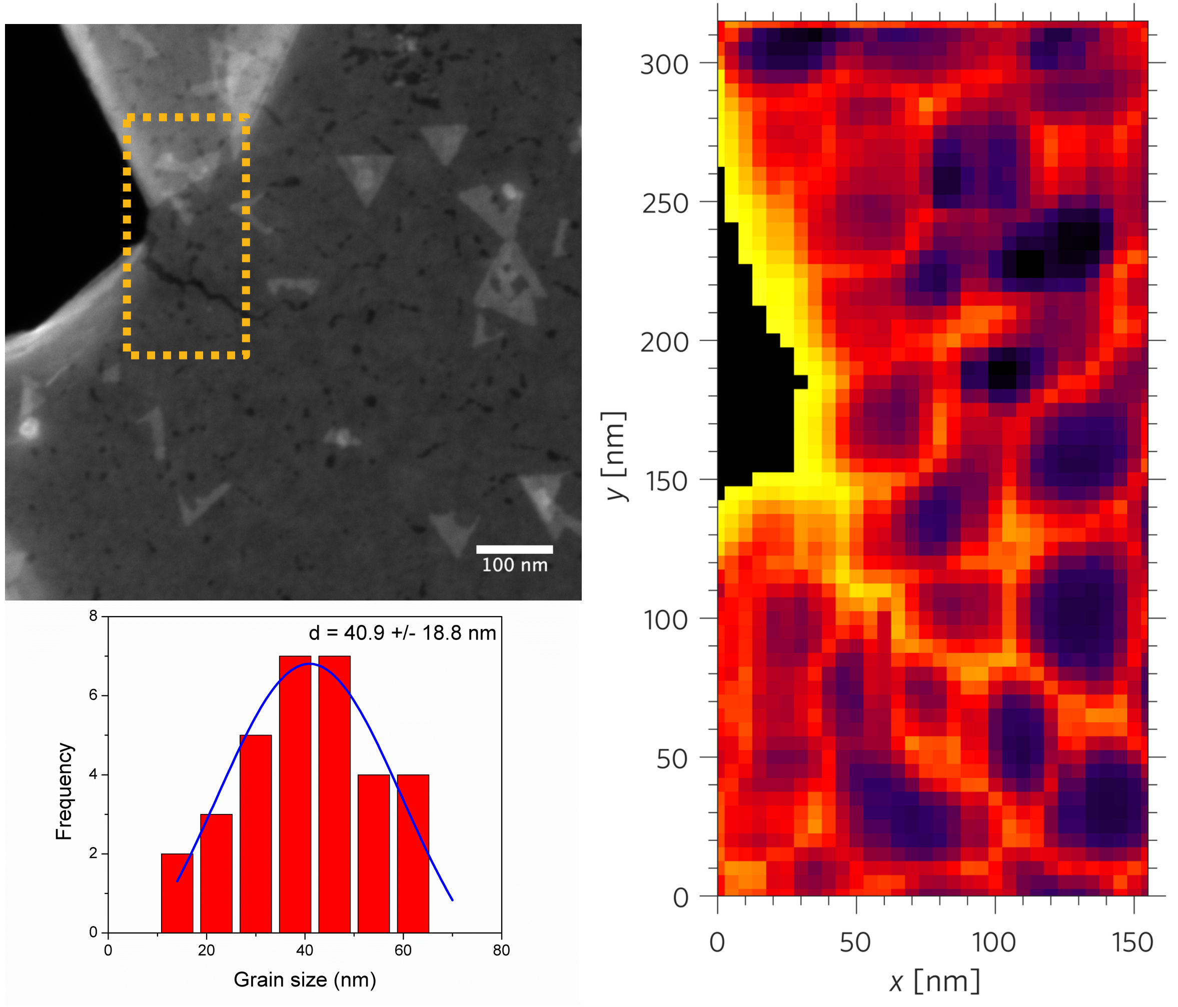


Recovered spatial information reveals grain boundary distribution

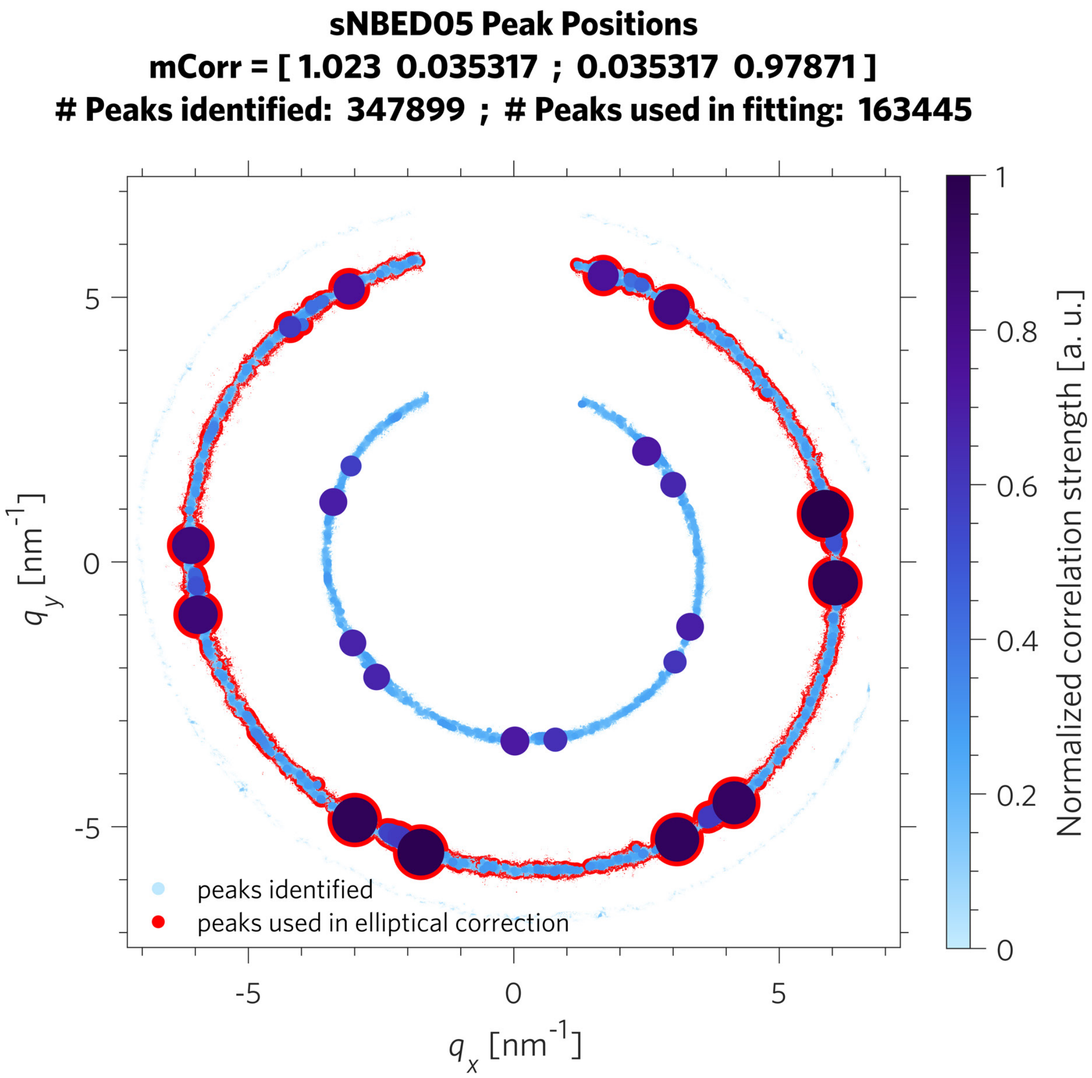
Ex. Sample 1



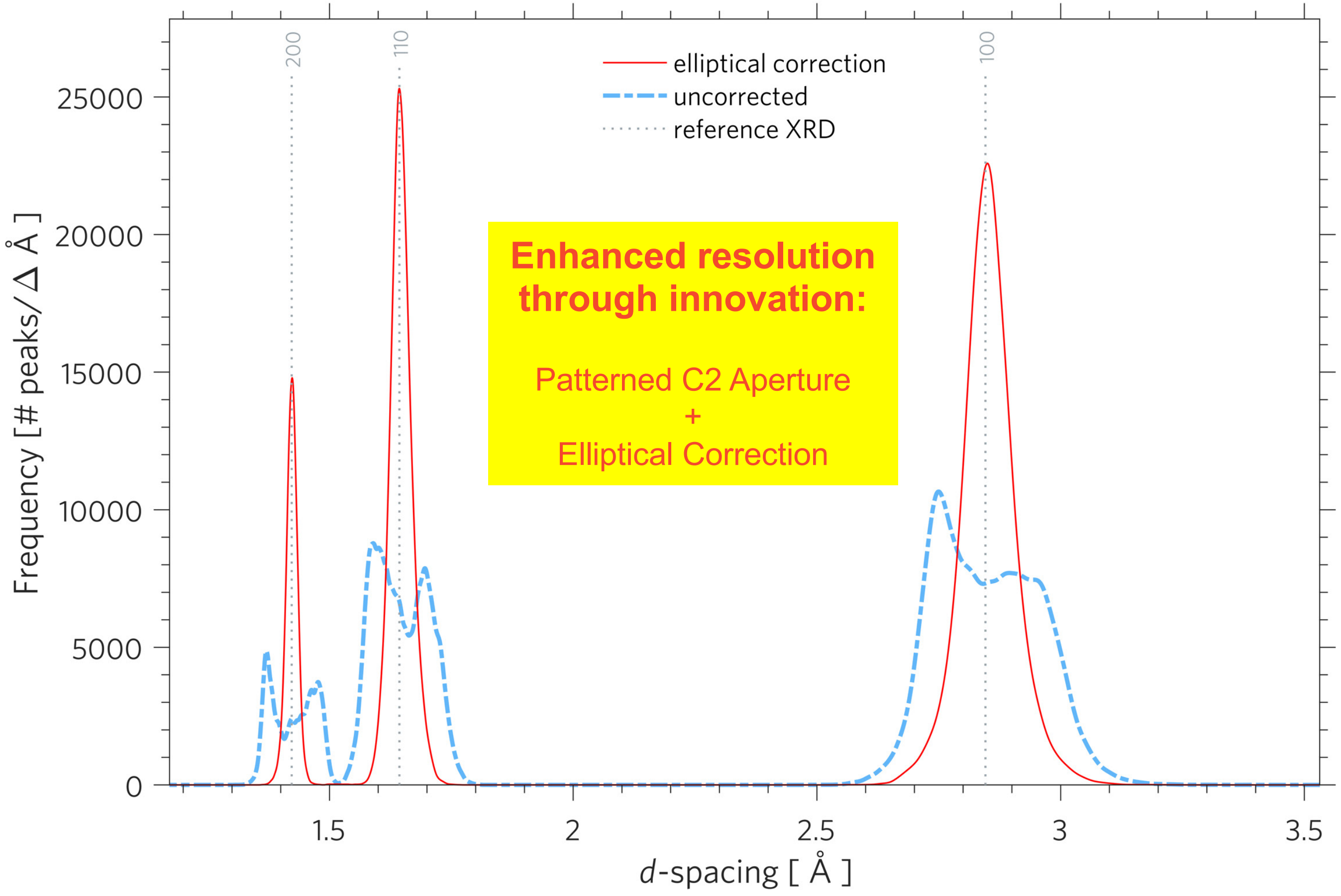
Ex. Sample 2



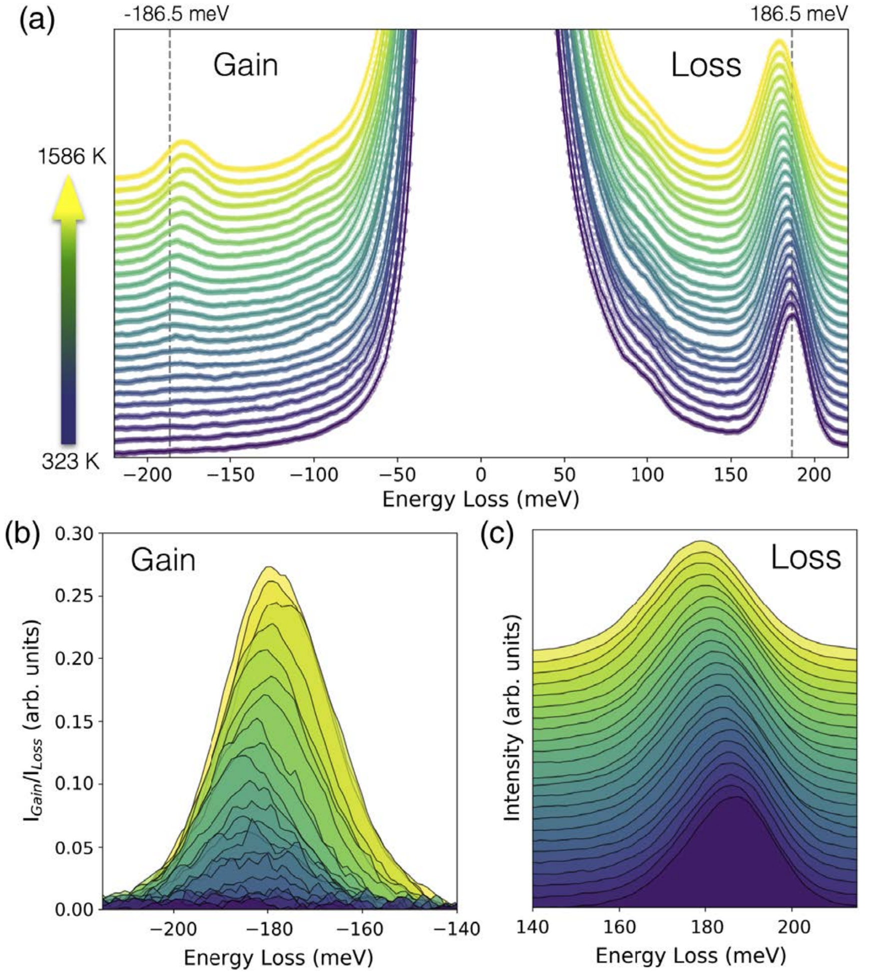
Elliptical correction matters for quantitative analysis



Located Peak Histogram



Comparison with alternate Electron Energy Loss Spectroscopic lattice expansion measurement techniques



Idrobo *et al.*, *Phys. Rev. Lett.* **2018**, *120*, 095901, https://doi.org/10.1103/PhysRevLett.120.095901

EELS plasmon shifts versus 4D STEM elastic scattering

- **Pros:**
  - Relatively simple if using correct instrument, Nion Company TEM (ORNL is leader in this)
- **Cons:**
  - No structural/crystallographic information
  - Already at ultimate temperature resolution of ~ 95 °C
  - Very expensive and specialized instrument made solely for maximizing energy resolution

Conclusions and Acknowledgments

Conclusions

Elastic strain engineering (*Nano Letters* **2018**, https://doi.org/10.1021/acs.nanolett.7b05229)

- We provided a new methodology for conducting strain-dependent experiments on thin materials and argue for adoption of a standard model for these studies.
- We reported a two orders of magnitude increase in the excitonic recombination rate of an indirect 2D material, bilayer WSe_2.

Localized defect emission (Feature Article, *Applied Physics Letters* **2019**, https://doi.org/10.1063/1.5091779)

- We developed a method to create highly-spatially localized and well-separated emission sites in a continuous film of WSe_2 using an ultra-sharp dielectric tip array, with $g^{(2)}(\Delta t=0) < 0.3$.
- May 2019 LANL science highlight: https://www.lanl.gov/discover/news-release-archive/2019/May/0529-quantum-information.php

Isotope effect (*Nano Letters* **2019**, https://doi.org/10.1021/acs.nanolett.8b04269)

- We demonstrated the isotope effect on the phonon frequency, phonon lifetime, and optical band gap energy in an atomically thin TMD through the use of naturally abundant and isotopically pure bilayer WSe_2.
- We postulated a new mechanism by which the electronic band gap energy and phonon dispersion can be tuned in this material by isotopic enrichment.
- April 2019 LANL science highlight: https://www.lanl.gov/discover/news-stories-archive/2019/April/0408-isotopic-composition.php
- MRS Bulletin: https://www.cambridge.org/core/journals/mrs-bulletin/news/isotope-composition-impacts-optical-spectrum-of-2d-bilayer-wse2

Acknowledgments

Elastic strain engineering

- **Pettes Lab:** Funding from NSF CAREER-1553987, NSF REU-1560098, UConn Foundation PD15-0067, FEI Graduate Fellowship, NSF GRFP
- **DFT:** Avinash Dongare, UConn MSE, funded by ARL W911NF-14-2-0059
- **TEM:** Peter Ercius, LBNL Molecular Foundry, funded by DoE DE-AC02-05CH11231

Localized defect emission

- **Pettes Lab:** Funding from DOE LDRD 20190516ECR, NSF CAREER-1553987, NSF REU-1560098, DOE DE-AC52-06NA25396, FEI Graduate Fellowship
- **Ion Beam Analysis:** Yongqiang Wang, LANL MST-8, funded by DOE 89233218CNA000001
- **Ultrafast Spectroscopy:** Joshua Hendrickson, AFRL/RY, funded by AFOSR FA9550-15RYCOR159
- **MOCVD:** Joan Redwing, Penn State MSE, funded by NSF DMR-1539916

Isotope effect

- **Pettes Lab:** Funding from DOE LDRD 20190516ECR, NSF CAREER-1553987, DOE DE-AC52-06NA25396
- **Ion Beam Analysis:** Yongqiang Wang, LANL MST-8, funded by DOE 89233218CNA000001

NBED strain mapping

- **Pettes Lab:** Funding from DOE LDRD 20190516ECR, LANL IMS Rapid Response Program RR19PETT, LANL ISTI Rapid Response Program RRDWPETTES
- **4DSTEM:** Colin Ophus and Rohan Dhall, LBNL Molecular Foundry, funded by DOE DE-AC02-05CH11231